Computational study of the mixed B-site perovskite SmB\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{3-d} (B = Mn, Fe, Ni, Cu) for next generation solid oxide fuel cell cathodes†

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SmCoO\textsubscript{3} is a promising perovskite material for the next generation of intermediate temperature solid oxide fuel cells (SOFC), but its potential application is directly linked to, and dependent on, the presence of dopant ions. Doping on the Co-site is suggested to improve the catalytic and electronic properties of this cathode material. Fe, Mn, Ni, and Cu have been proposed as possible dopants and experimental studies have investigated and confirmed the potential of these materials. Here we present a systematic DFT+U study focused on the changes in electronic, magnetic, and physical properties with B-site doping of SmCoO\textsubscript{3} to allow cathode optimization. It is shown that doping generally leads to distortion in the system, thereby inducing different electron occupations of the Co d-orbitals, altering the electronic and magnetic structure. From these calculations, the 0 K electronic conductivity (\(\sigma_e\)) was obtained, with SmMn\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{3} having the highest \(\sigma_e\), and SmFe\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{3} the lowest \(\sigma_e\), in agreement with experiment. We have also investigated the impact of dopant species and concentration on the oxygen vacancy formation energy (\(E_i\)), which is related to the ionic conductivity (\(\sigma_i\)). We found that the \(E_i\) values are lowered only when SmCoO\textsubscript{3} is doped with Cu or Ni. Finally, thermal expansion coefficients were calculated, with Mn-doping showing the largest decrease at low \(x\) and at \(x = 0.75\). Combining these results, it is clear that Mn-doping in the range \(x = 0.125–0.25\) would imbue SmCoO\textsubscript{3} with the most favorable properties for IT-SOFC cathode applications.

1. Introduction

Solid oxide fuel cells (SOFC) are low-emission, high efficiency electrical generators, which show great promise as an emerging energy technology.\textsuperscript{1,2} However, in order to decrease costs and to prolong cell lifetimes, a concerted research effort is required to lower SOFC operating temperatures into the temperature range 500–800 °C.\textsuperscript{2,3} Unfortunately, traditional cathode materials such as La\textsubscript{0.6}Sr\textsubscript{0.4}MnO\textsubscript{3-\delta} (LSM), which has long been the state-of-the-art SOFC cathode, have been shown to be inefficient under these operating conditions.\textsuperscript{4,5} It is the main task of the cathode to catalyze the oxygen reduction reaction (ORR) and facilitate oxygen diffusion through the electrolyte towards the anode. To this end, it should have high electronic conductivity (\(\sigma_e\)), which depends on the electronic structure, and ionic conductivity (\(\sigma_i\)) which is dependent on the concentration of oxygen vacancies (\(V_0\)) and therefore on the oxygen vacancy formation energy (\(E_i\)).\textsuperscript{1,3,6} The cathode should further be chemically and physically compatible with the coupled electrolyte. Hence, having thermal expansion coefficients (TEC) close to those of traditional electrolytes (10–13 × 10\textsuperscript{-6} K\textsuperscript{-1}) is important to minimize strain in the cell to prevent premature failure.\textsuperscript{7}

In view of the above, new cathode materials are sought, which has led to interest in cobalt-based cathodes.\textsuperscript{8} These materials have shown excellent SOFC cathode properties at intermediate temperatures, with high \(\sigma_i\) and \(\sigma_e\).\textsuperscript{9} A promising
material is SmCoO$_3$, which is in itself a semiconductor, but by dop- ing this perovskite on the Co-site with manganese, nickel, iron, or copper, $\sigma_{\text{d}}$ can be increased through modification of its electronic structure.\textsuperscript{9–12} Such doping makes SmCoO$_3$ a p-type semiconductor, and samarium oxide perovskites doped with transition metals on the B sites, show excellent promise as intermediate temperature (IT-SOFC) cathodes.\textsuperscript{13} Fullarton et al. discovered that partial substitution on Sm (with Sr and Ca) and/or Co (with Ni, Cu, and Fe) sites in SmCoO$_3$ greatly improves $\sigma_{\text{d}}$.\textsuperscript{14} In combination with doping on the Sm site, substitutional Co-site doping of SmCoO$_3$ with other transition metals has the potential to increase $\sigma_{\text{d}}$ by making the materials metallic and magnetic, as well as having an impact on the TEC which decreases.\textsuperscript{10,15} For example, Mn-doping of SmCoO$_3$-type cathode materials has been shown experimentally to decrease the TEC, alter the catalytic properties, and increase conduction – property changes that have also been shown for La-based materials.\textsuperscript{15,28–30} Mentally to alter the electronic conduction, and be capable of incorporating, and the catalytic oxygen reduction activity has also been shown to readily reduce the TEC of SmCoO$_3$-based cathode materials.\textsuperscript{13,16}

However, the full substitution of Co by dopants leads to completely different types of perovskite materials (SmBO$_x$), which, compared to LaBO$_x$, have been subject to few experimental and only some theoretical studies. Previous computational research has focused on SmFeO$_3$\textsuperscript{47–20} and SmMnO$_3$\textsuperscript{21,22} whereas computational information on SmNiO$_3$ and SmCuO$_3$ is scarce.\textsuperscript{23–27} However, experimental studies exist, providing the basis for this study,\textsuperscript{15,28–30} where both Ni and Cu are proposed to readily decrease the TEC in SOFC cathodes, and to be possible dopants in SmCoO$_3$.\textsuperscript{14,25}

Taking into account previous work and the promise of SmCoO$_3$ as an IT-SOFC cathode material, here we present a systematic study on the doping of SmCoO$_3$ with Mn, Fe, Ni, and Cu at different concentrations, as well as the fully substituted SmBO$_3$ pseudo-cubic structures. We pay special attention to the effect of the dopant concentrations on the geometric, electronic and magnetic structures, as well as the electronic and ionic conductivities. In addition, the energetics and electronic implications of the oxygen vacancy formation is also investigated. Each of these data points are combined to allow the optimization of properties for B-site doping of SmCoO$_3$.

2. Computational details

2.1 Density functional theory (DFT) calculations

All calculations except for the thermal expansion, discussed below, in this study employed the Vienna ab initio simulation package (VASP, version 5.3.5).\textsuperscript{31–34} We have applied the projector-augmented wave method (PAW) to describe the ion-electron interaction,\textsuperscript{35} and, based on convergence tests, the energy cut-offs for all systems were set to 500 eV. Spin-polarized calculations were executed using the Perdew–Burke–Ernzerhof (PBE)\textsuperscript{36,37} functional under electronic (convergence criterion of 10$^{-7}$ eV) and ionic (convergence criterion of 10$^{-3}$ eV Å$^{-1}$) self-consistence. The following valence electrons were considered for the atomic species involved: Sm (5s$^2$5p$^6$6s$^2$), Mn (3p$^6$3d$^5$4s$^2$), Fe (3p$^6$3d$^5$4s$^2$), Co (4s$^2$3d$^7$), Ni (4s$^2$3d$^8$), Cu (4s$^1$3d$^{10}$) and O (2s$^2$2p$^4$).

Furthermore, the tetrahedron method with Blochl corrections for smearing\textsuperscript{38} was applied, together with a 4 × 4 × 4 Γ-centered Monkhorst–Pack grid.\textsuperscript{39} Bader AIM (Atoms in Molecules) charges\textsuperscript{40} were calculated using the Henkelman algorithm.\textsuperscript{41} The supercell used throughout this work is the 2 × 2 × 2 Pm3m pseudo-cubic cell, as this was found to be large enough to model bulk properties and defect structures within reasonable computational resources.

To describe electronic structures, we have used the on-site coulombic interaction (DFT+U) for the B 3d-electrons. Normal exchange correlation functionals (LDA or GGA) cannot correct the electron self-interaction problem, leading to a metallic description of perovskites or at least an underestimation of their band gaps.\textsuperscript{42–44} In this work, we have employed Dudarev’s approach,\textsuperscript{45} in which an effective Hubbard parameter (U$_{\text{eff}}$) is applied to the B d-states. The U$_{\text{eff}}$-parameters for B ions in perovskites have been extensively fitted and tested elsewhere, based on lattice parameters, band gaps and properties such as magnetic structures, enthalpy of formation, and defect formation energies. Based on this prior work, here we have used the following Hubbard parameters: U$_{\text{eff}}$ = 4 eV\textsuperscript{46} for Mn, U$_{\text{eff}}$ = 4.3 eV\textsuperscript{47} for Fe, U$_{\text{eff}}$ = 3 eV\textsuperscript{48} for Co, U$_{\text{eff}}$ = 6.4 eV\textsuperscript{46} for Ni, and U$_{\text{eff}}$ = 3 eV\textsuperscript{49} for Cu. The electronic conductivity is calculated for the 0 K optimized electronic structures from the frequency dependent dielectric matrix, where the electronic conductivity can be calculated from the dielectric constant, dielectric loss factor, and the loss tangent, which are then obtained from the dielectric parameters.\textsuperscript{50–53}

2.2 Molecular dynamics (MD) simulations

Thermal expansion coefficients were calculated from molecular dynamics (MD) simulations using the DL_POLY 4 program.\textsuperscript{54} 20 × 20 × 20 supercells based on the DFT+U optimized SmB$_2$Co$_{1–x}$O$_3$ structures were simulated under NPT conditions (constant number of particles, pressure and temperature), with a Nose–Hoover thermostat.\textsuperscript{55} All statistics were collected after a 10 ps system equilibration, with a 100 ps production phase and a time step of 0.1 fs. To account for electrostatic interactions, the Ewald summation was employed, and the Verlet algorithm was employed to evaluate the atomic motions. Short-range atomic interactions were calculated with Buckingham potentials (eqn (1)), which are used extensively within the Born model for ionic solids.\textsuperscript{56–58} Eqn (1) shows the Buckingham potential expression, with $r$ defining the distance between ions $i$ and $j$, and $A$, $\rho$, and $C$ being empirically fitted parameters.

$$V_{ij}(r) = A \exp \left( -\frac{r}{\rho} \right) - \frac{C}{r^6} \quad (1)$$

To describe the electronic polarization of the atoms ($\delta$), the shell model is included,\textsuperscript{48,59} where ions are modelled as cores,
connected by a harmonic spring ($k$) to a massless shell with charge $Y$ (eqn (2)).

$$x = \frac{y^2}{k}$$  \hspace{1cm} (2)

The relevant interatomic potentials are taken from the Cherry et al. library, as these have previously been used to model $\sigma_0$ in perovskites,\textsuperscript{60} and have already been evaluated for SmCoO$_3$.\textsuperscript{61} The full set of interatomic potentials is presented in Table S1 in the ESI.$^\dagger$

### 3. Results and discussion

#### 3.1 Dopant configuration

As a first step, the non-equivalent dopant configurations in SmB$_2$Co$_{1-x}$O$_3$ were evaluated using the Site-Occupancy Disorder Program (SOD).\textsuperscript{62} The $2 \times 2 \times 2$ supercell includes eight Co lattice positions, thus a substitution of one Co by a dopant ion B represents a dopant concentration of $x = 0.125$ (for which only one non-equivalent structure can be found), for two Co substitutions $x = 0.25$, four substitutions $x = 0.50$, and finally in $x = 0.75$ we have two Co and six B. Three inequivalent configurations exist for $x = 0.25$ and 0.75, and six for $x = 0.5$. The different SmB$_2$Co$_{1-x}$O$_3$ configurations were optimized with VASP, with their relative energies collected in Table S2 of the ESI,$^\dagger$ after which the lowest energy configurations were selected for further study (Fig. 1). In real systems, a degree of disorder between dopant configurations would be expected. However, in order to avoid confusion, and as the smallest energy difference between the different dopant configurations for any particular dopant and dopant level was more than 0.1 eV, only the lowest energy configurations have been considered here. It was found that the lowest energy dopant configurations were dependent on both the dopant type and dopant configuration.

In order to further understand the trends in doped SmB$_2$Co$_{1-x}$O$_3$, we have also studied the SmBO$_3$ perovskites. Cubic SmBO$_3$ perovskites are isostructural, with differences in the B–O bond lengths ranging from 0 to 0.6 Å related to the differences in B ionic radii between the materials (Table S3 in ESI$^\dagger$). As a result, variations in lattice parameter are observed over the periodic series (Table 1), according to the nature of B, in terms of ionic radii and electronegativity, which will influence the chemistry and physical properties of these materials.

#### 3.2 Electronic and magnetic structures

Co and B can exist in different spin states, depending on the d-orbital occupation. Co$^{3+}$ (3d$^6$) has a low-spin ground state (LS, $t_{2g}^0e_g^0$), and a negligible magnetic moment ($\mu$) of 0 $\mu_B$.\textsuperscript{63} However, upon distortion of the CoO$_6$-octahedra, the d-orbital occupation can be altered, resulting in different spin states, specifically intermediate (IS, $t_{2g}^1e_g^1$) or high (HS, $t_{2g}^4e_g^2$) states, thus modifying the magnetic properties of the system.\textsuperscript{64} In addition, the dopants considered in this work can also present different d-orbital occupations and consequently different spin states.\textsuperscript{46,65}

#### 3.3 Lattice parameter variations

In order to further understand the trends in doped SmB$_2$Co$_{1-x}$O$_3$, we have also studied SmBO$_3$, with relative energies collected in Table S2 of the ESI.$^\dagger$ SmFeO$_3$ was found to have a C-AFM ground state, with G-AFM being the energetically second-most stable configuration, found to be 0.11 eV per formula unit higher in energy. For SmMn$_2$O$_3$ and SmNiO$_3$, FM configurations are more stable than AFM, where in both cases the difference in energy to the second-most stable magnetic structure was more than 0.4 eV per formula unit, in agreement with previous data on cubic phase lanthanide manganate perovskites, and cubic SmNiO$_3$ (which undergoes an insulator-to-metal transition at $\sim$ 400 K).\textsuperscript{15,66} Finally, for SmCuO$_3$, our calculations could only obtain the FM and NM structures, and, according to their relative energies, this material is expected to be non-magnetic, with the FM structure 0.66 eV per formula unit higher in energy.

For SmMn$_2$Co$_{1-x}$O$_3$, regardless of the dopant concentration, an overlap between the Co and Mn $e_g$-bands (Fig. 2) is always found at the Fermi level, anticipating a high electron conductivity,
Table 1  Lattice parameter (\(a\)) in Å, local magnetic moments (\(\mu\)) in \(\mu_B\) for cobalt and dopant, band gap (\(E_g\)) in eV, and magnetic ordering in Sm\(_3\)Co\(_1-x\)O\(_3\). The magnetic moments of samarium and oxygen were found to be negligible in relation to the transition state metals. \(a\) for SmCoO\(_3\) is 3.75 Å. \(q_{Co}\) in SmCoO\(_3\) is 1.31 e\(^-\). A full list of Bader charges for each system is included in Table S4 in the ESI.

<table>
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<tr>
<th>B</th>
<th>(x = 0.125)</th>
<th>(x = 0.25)</th>
<th>(x = 0.5)</th>
<th>(x = 0.75)</th>
<th>(x = 1.0)</th>
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<td>(a)</td>
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<td>1.74</td>
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<tr>
<td></td>
<td>(q_{Co})</td>
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<td>1.25</td>
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<td>1.13</td>
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<td>0 ((z), 0.97 ((\beta))</td>
<td>0 ((z), 1.66 ((\beta))</td>
<td>0 ((z), 2.16 ((\beta))</td>
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<td>4.3</td>
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<td>(q_{Fe})</td>
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<td>1.17</td>
<td>1.18</td>
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<td>(E_g)</td>
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<td>0.46 ((z), 0 ((\beta))</td>
<td>2.23 ((z), 1.67 ((\beta))</td>
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<td>0.6</td>
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<td>1.25</td>
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<td>1.34, 1.24</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
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<td>1.02 ((z), 0 ((\beta))</td>
<td>0 ((z), 0.67 ((\beta))</td>
<td>0.06 ((z), 0.21 ((\beta))</td>
</tr>
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</table>

as high \(\sigma_c\) has been reported to go through \(e_g\)-bands.\(^{67,68}\) The contribution of each band depends on the dopant concentration, with larger contributions of the Co \(e_g\)-bands at lower dopant concentrations, and \(vice versa\) when the material is heavily doped. Increasing the dopant concentration does not affect the Co \(t_{2g}/e_g\)-splitting. We know from previous publications that the change in the spin state, and thus the occupation of the d-orbitals in Co, can be directly related to the distortion of the octahedral environment, \(i.e.\) distortions in the Co–O bonds.\(^{64}\) Indeed, for \(x = 0.125\), \(x = 0.25\) and \(x = 0.75\), these bonds are only distorted by \(\approx 0.01\) Å with respect to the ideal Co–O bond of 1.88 Å. However, for \(x = 0.5\), the range of Co–O bond lengths is wider (1.88–1.95 Å), thus altering the Co d-orbital crystal field splitting, and consequently, the orbital occupation.

This exception for \(x = 0.5\) can also be observed in the variation of the cobalt magnetic moment. As shown in Table 1, \(\mu_{Co}\) is close to 0 for all concentrations, with the exception of \(x = 0.50\) with a \(\mu_{Co}\) of 2.4 that can be associated to an intermediate spin (IS) state. This behavior is also observed in the PDOS, with the occupation of the Co \(e_g\)-orbitals on the one hand and \(\beta-t_{2g}\)-orbitals at positive energies on the other. Moving through the PDOS with increasing \(x\), it can be seen that this material becomes gradually more like SmMnO\(_3\). The \(\beta\)-band gap increases with increasing \(x\), reaching a maximum in SmMnO\(_3\). Also noticeable is the magnetic moment of Mn, which is found to be between 3.76 and 3.85, indicating that Mn is found in its higher spin state, with the highest Mn magnetic moment observed in SmMnO\(_3\). Furthermore, \(\mu_{Mn}\) decreases with decreasing Mn-content \(\langle x_{Mn}\rangle\), a behaviour that has been observed previously in LaMn\(_1-x\)CoO\(_3\).\(^{69}\)

The crystal field splitting for cobalt is further observed to remain unchanged with increasing Fe concentration (Fig. 2), which is mainly due to the low degree of distortion suffered by the Co–O bonds upon Fe-doping, as can be seen in Table S3 of the ESI. At \(x = 0.125\), Fe-doped SmCoO\(_3\) is metallic, with an overlap of Fe \(e_g\)- and Co \(t_{2g}\)-bands at the Fermi level, where we thus may expect a relatively large electronic conductivity. However, with increasing dopant concentration, the material becomes increasingly semiconducting, disqualifying it as a good cathode candidate. As was observed for SmMn\(_3\)Co\(_1-x\)O\(_3\), SmFe\(_3\)Co\(_1-x\)O\(_3\) gains more SmFeO\(_2\) character with increasing \(x\), with the band gap becoming increasingly symmetrical, resulting in pure semi-conductor behaviour at \(x = 1.0\). On the other hand, the iron magnetic moment remains mostly constant over the series at 4.2 \(\mu_B\), whereas the Co magnetic moments are very low for the entire series, oscillating between 0.0 and 0.4 \(\mu_B\). In SmFeO\(_3\), all Fe–O bond lengths are equal, which results in a symmetrical electronic structure. It is worth noting that all Fe–O bonds are equal for \(x = 0.5\) as well, but the Co–O bond lengths, whilst all the same, are different to the Fe–O bonds, thus inducing distortions in the oxygen sublattice resulting in an asymmetric PDOS.

The electronic structures of SmNi\(_3\)Co\(_1-x\)O\(_3\) and SmCu\(_3\)Co\(_1-x\)O\(_3\) show different behaviour to the Fe- and Mn-doped systems.
In SmNi$_{x}$Co$_{1-x}$O$_{3}$, the Co t$_{2g}$-bands are not fully occupied whereas the e$_g$-bands are partially occupied, which can be related directly to a change in the Co spin moment, and thus to the changes in the Co-O distances (Table S3, ESI†). Interestingly, for $x = 0.125$ the system is a conductor, but conduction occurs only through the Co t$_{2g}$-bands and as soon as the dopant concentration increases, the system becomes half-metallic and the conduction occurs through the nickel e$_g$-bands. The half-metallic nature is preserved in SmNiO$_3$, thus inferring that Ni-doping, even at low concentrations, induces

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**Fig. 2** Projected density of states (PDOS) for SmB$_x$Co$_{1-x}$O$_3$. The Fermi level is at 0 eV for all representations, where negative values represent the occupied bands and positive values represent the virtual bands. In addition, positive PDOS are associated to the $\alpha$-spin whereas negative PDOS are associated to $\beta$-spin. Note that the Mn, Fe, Ni, and Cu PDOS have been multiplied by a factor of 10 for $x = 0.125$, 5 for $x = 0.25, 0.5$, and by 2 for $x = 0.75$. 
more SmNiO$_3$-type behavior than SmCoO$_3$-type. It is worth noting that there is no overlap between the bands of Co and Ni, which is indicative of poor electronic conductivity.

For SmCu$_x$Co$_{1-x}$O$_3$ (Fig. 2), the Cu $e_g$-bands are partially occupied over the Fermi level for $x = 0.125$, $x = 0.25$ and $x = 0.5$, indicating that electronic conductivity should be possible. For $x = 0.75$, a change in the electronic structure is seen around the Fermi level, resulting in a small band gap, which would suggest a decrease in $\sigma_e$. For SmCuO$_3$, the electronic structure becomes fully metallic and ferromagnetic. Additionally, for all $x_{Cu}$ the cobalt octahedral environment is distorted, resulting in the Co $t_{2g}$-levels splitting over the valence and conduction bands, which again can be related directly to a change in the cobalt spin moment, and thus to distortions in the Co–O distances, as listed in Table S3 (ESI†).

Moreover, Bader charges and magnetic moments for cobalt at different concentrations suggest the presence of different mixed valence states, for example when $x = 0.125$. In this situation, Co charges decrease and increase by $\sim 0.2$ e with respect to the Co charge in SmCoO$_3$. This difference could be seen as a partial change in oxidation state, but neither the magnetic moments nor the electronic structure are clear enough to support this idea. On the other hand, nickel’s magnetic moment is around 1.7 for all concentrations, indicating that nickel is found in a mixed spin state.

#### 3.2.1 Electronic conductivity ($\sigma_e$)

It is generally accepted for SOFC cathodes that a high electronic conductivity ($\sigma_e$) is required for good cathode performance. Here, we have calculated the electronic conductivities for all the aforementioned Sm$_{1-x}$Co$_x$O$_3$ at 0 K (Table S6 in ESI† and Fig. 3). Although thermal effects may alter the electronic conduction, as we strive to study relevant trends due to dopant effects, the 0 K electronic conduction is a suitable first approximation. From these results, it is clear that in SmFe$_{0.5}$Co$_{0.5}$O$_3$, $\sigma_e = 0$ S cm$^{-1}$ for $x > 0.125$, as expected considering that the PDOS revealed that the material becomes semi-conducting. It is known from experimental data that Fe-containing perovskites generally have lower $\sigma_e$ than those containing manganese, and that $\sigma_e \neq 0$ S cm$^{-1}$ in Fe-based perovskites at temperatures above 200 °C. Thus, it is reasonable to suggest that at elevated temperatures, $\sigma_e$ will increase for this material, although this increase in $\sigma_e$ is not expected to be remarkable in comparison to other systems modelled here. Focusing on those systems with the highest $\sigma_e$, i.e. SmMn$_{0.125}$Co$_{0.875}$O$_3$, SmMn$_{0.25}$Co$_{0.75}$O$_3$, SmFe$_{0.125}$Co$_{0.875}$O$_3$, and SmNi$_{0.25}$Co$_{0.75}$O$_3$, it is seen that Cu-doping would not represent a major improvement in terms of $\sigma_e$ since the maximum $\sigma_e$ that can be obtained is at $x = 0.25$ with a $\sigma_e$ of 120 S cm$^{-1}$.

The largest $\sigma_e$ are obtained for SmMn$_{0.125}$Co$_{0.875}$O$_3$ and SmFe$_{0.125}$Co$_{0.875}$O$_3$. These large $\sigma_e$ can be attributed to the overlapping between the d-bands of Co and the dopants. It is further expected that at higher temperatures, these $\sigma_e$ could be increased. Moreover, all $\sigma_e$ are in line with general IT-SOFC cathode requirements and experimentally obtained data.

#### 3.3 Hole and oxygen vacancy formation

A critical property for SOFC cathodes is their high combined electronic and ionic conductivity. Mixed ionic and electronic conductors (MIECs) have electronic conductivity (as presented above) reinforced by ionic conductivity. Ionic conductivity in these perovskites proceeds via an oxygen vacancy hopping mechanism, inferring that a high concentration of oxygen vacancies is important. Oxygen vacancies are generally formed as the result charge compensation, but can also be formed as a function of oxygen partial pressure and temperature. Furthermore, it has been demonstrated that hole formation could lead to higher electronic conductivity. Hence, we below investigate both hole and oxygen vacancy formation in SmB$_{3-x}$Co$_x$O$_3$.

#### 3.3.1 Hole formation

Perovskite oxides are known to be able to accommodate hole polarons, which have been identified in other perovskites such as SrTiO$_3$, and manganese in particular is known to be prone to form electron–hole pairs. Hole formation energies can be calculated as the difference in total energy between the fully relaxed localized polaron state, and the delocalized hole state in the undistorted lattice. Using this formulation, a large negative hole formation energy indicates that the relaxed structure is more energetically stable than the unrelaxed hole. Hence, the energetic difference represents the energy gained on hole localization, shown in Table 2.

<table>
<thead>
<tr>
<th>B</th>
<th>$x = 0.125$</th>
<th>$x = 0.25$</th>
<th>$x = 0.5$</th>
<th>$x = 0.75$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>-0.13</td>
<td>-0.23</td>
<td>-0.47</td>
<td>-0.15</td>
</tr>
<tr>
<td>Fe</td>
<td>-1.28</td>
<td>-0.27</td>
<td>-0.40</td>
<td>-1.39</td>
</tr>
<tr>
<td>Ni</td>
<td>-0.66</td>
<td>-1.03</td>
<td>-1.27</td>
<td>-1.07</td>
</tr>
<tr>
<td>Cu</td>
<td>-1.12</td>
<td>-0.79</td>
<td>-1.02</td>
<td>-0.13</td>
</tr>
</tbody>
</table>
Hence, the hole polarons formed in these systems represent the deep hole states that would be expected to remain localized at device operating temperatures. Mn-doping on the other hand leads to much smaller hole formation energies, which is in line with previous work on manganese-based perovskites.\textsuperscript{72} The hole formation in Mn-containing systems has been assigned to the breakdown of the Mn\textsuperscript{3+} charge state to Mn\textsuperscript{2+} and Mn\textsuperscript{4+}, which furthermore leads to high electronic conductivity as these states are shallow and hence mobile at elevated temperatures.\textsuperscript{72}

### 3.3.2 Oxygen vacancy formation

Oxygen vacancies influence the bulk ionic conduction in SOFC cathode materials, and thus it is important to assess the effect of the dopants on the oxygen vacancy formation. The SOD program\textsuperscript{62} was utilized to introduce a single oxygen vacancy (V\textsubscript{O}) in all systems, and the models were then optimized using VASP. The oxygen vacancy formation energy (\(E_f\))\textsuperscript{79} with lower \(E_f\) indicating higher \(V_O\) concentration (\(C_O\)) at equilibrium conditions,\textsuperscript{48} is calculated according to eqn (3) and (4),

\[
E_f = E_{\text{Defective}} - E_{\text{Bulk}} + \mu_O \tag{3}
\]

\[
\Delta \mu_O = \mu_O - \frac{g_{O_2}^{\text{tot}}}{2} \leq 0 \tag{4}
\]

where \(k_B\) is the Boltzmann constant, \(T\) the temperature, \(E_{\text{Defective}}\) the total energy of the system with \(V_O\), \(E_{\text{Bulk}}\) the total energy of the bulk, and \(\mu_O\) is the oxygen chemical potential.\textsuperscript{80-85} \(\Delta \mu_O\) is the oxygen chemical potential deviation, and \(g_{O_2}^{\text{tot}}\) is the free energy of the oxygen molecule (\(O_2\)).\textsuperscript{80-85} It is widely accepted that \(g_{O_2}^{\text{tot}}\) can be approximated by the DFT energy of \(O_2\) (\(E_0\)) when calculations are performed under oxygen-rich conditions, and the material is in thermodynamic equilibrium with the surface, and that the latter is in equilibrium with the gas phase.\textsuperscript{83} However, it is necessary to determine first whether the material is stable or not for \(\Delta \mu_O = 0\), which is evaluated through chemical potential phase diagrams. A more detailed explanation on how to construct these diagrams can be found in the ESI.\textsuperscript{†}

#### 3.3.2.1 Oxygen vacancy formation in Sm\(_{1-x}\)Co\(_x\)O\(_3\). For SmCo\(_{1-x}\)O\(_3\), it was shown in our previous work that the upper limit to \(\Delta \mu_O\) is --0.5 eV.\textsuperscript{48} In this work, we thus constructed phase diagrams for SmMnO\(_3\) and SmFeO\(_3\), from which we found that the upper limits of the oxygen potential (eqn (4)) for SmMnO\(_3\) (based on experimental data from Pawlas-Foryst et al.)\textsuperscript{86} is \(\Delta \mu_O \leq 0\) eV, whereas for SmFeO\(_3\) (based on experimental data from Parida et al.)\textsuperscript{86} it is \(\Delta \mu_O \leq --0.7\) eV. The lack of experimental data for SmCuO\(_3\) and SmNiO\(_3\) meant that we could not calculate their respective phase diagrams, although it has been reported that both materials are unstable under high partial oxygen pressures.\textsuperscript{24,26,27}

As such, for ease of comparison \(\Delta \mu_O = --0.5\) eV has been used for all materials and concentrations, and we have assumed that the ensuing error for SmFeO\(_3\) is negligible for the purpose of this discussion.\textsuperscript{13,48} However, we have considered \(\Delta \mu_O = 0\) for SmMn\(_{0.75}\)Co\(_{0.25}\)O\(_3\) since its stoichiometry is closer to SmMnO\(_3\) than it is to SmCoO\(_3\).

#### 3.3.2.2 Oxygen vacancy formation in SmBO\(_3\).

Comparison of \(E_f\) in SmBO\(_3\) is presented in Fig. 4. SmBO\(_3\) show a non-linear \(E_f\) trend (comparable to LaBO\(_3\))\textsuperscript{4,66} with Fe-based lanthanide oxides having the highest \(E_f\). What is notable in comparison with LaBO\(_3\)\textsuperscript{4,66} is that the trend is more extreme, where \(E_f\) for SmFeO\(_3\) is higher by \(\sim 1\) eV, whereas \(E_f\) for SmMnO\(_3\) and

Table 3

<table>
<thead>
<tr>
<th>B</th>
<th>(x = 0.125)</th>
<th>(x = 0.25)</th>
<th>(x = 0.5)</th>
<th>(x = 0.75)</th>
<th>(x = 1.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>1.77</td>
<td>1.85</td>
<td>2.06</td>
<td>2.20</td>
<td>2.36</td>
</tr>
<tr>
<td>Fe</td>
<td>1.82</td>
<td>2.20</td>
<td>3.03</td>
<td>1.49</td>
<td>5.65</td>
</tr>
<tr>
<td>Ni</td>
<td>1.66</td>
<td>1.09</td>
<td>2.15</td>
<td>0.44</td>
<td>0.55</td>
</tr>
<tr>
<td>Cu</td>
<td>1.69</td>
<td>0.55</td>
<td>0.79</td>
<td>0.42</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Comparing the oxygen vacancy formation energies with respect to undoped SmCoO\(_3\) (2.08 eV), Co-site doping with B does not markedly lower \(E_f\) except when doped with Cu, and at \(x_{Ni} > 0.75\). The calculated oxygen vacancy formation energies for Ni- and Cu-doped SmCoO\(_3\) (Table 3, and Table S7 in ESI) indicate -- in agreement with experimental studies\textsuperscript{15,24,26,27} -- that only SmNi\(_{1-x}\)O\(_3\)-doped and SmCu\(_{1-x}\)O\(_3\)-doped lead to meaningful reduction in the \(V_O\) formation energy at higher dopant concentrations. As such, these systems are expected to be oxygen-deficient at IT-SOFC operating temperatures and oxygen partial pressures. However, the effect of Co-site doping on the \(V_O\) formation energies is limited when compared to Sm-site doping, where spontaneous formation of oxygen vacancies are observed. Sm-site doping reduces the oxygen vacancy formation energy by more than 2.5 eV,\textsuperscript{82} whereas the maximum reduction in oxygen vacancy formation energy seen here is 1.66 eV. Hence, this doping scheme has a much larger effect on the electrical conductivity than the ionic conductivity. This finding is in accordance with B-site doping having a limited effect on \(\sigma_{Iv}\) with a much larger impact seen from Sm-site doping.

![Fig. 4](image_url)  
Oxygen vacancy formation energy as a function of transition metal ion in SmBO\(_3\) (B = Mn, Fe, Co, Ni, and Cu). Solid line SBO is SmBO\(_3\), and dashed line LBO is LaBO\(_3\) with the values taken from Lee et al.\textsuperscript{66}
SmCoO$_3$ is lower. $E_f$ in SmNiO$_3$ and SmCuO$_3$ are very low, as was also seen for SmCu/Ni$_{1-x}$Co$_x$O$_3$. These low $E_f$ are a consequence of the instability of the Ni and Cu 3+ oxidation state, as was observed previously in LaNiO$_3$ and LaCuO$_3$. To investigate the impact of V$_0$ formation on the charge distribution in SmBO$_3$, we have plotted the change in spin density ($\Delta \rho_{x-\beta}$) upon V$_0$ formation (Fig. 5) as

$$\Delta \rho_{x-\beta} = \rho_{SmBO_{3-x}} - \rho_{SmBO_3} - \rho_{O}$$

$\Delta \rho_{x-\beta}$ shows clearly that in all SmBO$_3$, apart from SmFeO$_3$, $\text{B}^{2+}$–$\text{V}_0$–$\text{B}^{2+}$ clusters are formed, indicated by the gain in $\Delta \rho_{x-\beta}$ on the B-sites. This is most clearly evident in SmMnO$_3$, whereas in SmNiO$_3$ and SmCuO$_3$ some additional $\Delta \rho_{x-\beta}$ is located on the oxygen (in the same plane as V$_0$) nearest to the reduced copper and nickel ions. In SmFeO$_3$, which is the compound that stands out most in this series with the highest $E_f$, the C-AFM structure is kept, whereas the lattice is distorted, and there is a general change in spin throughout all Fe-sites. The magnetic moments and Bader charges on the neighboring Fe ions have been reduced from $\mu_{Fe} = 4.2$ to $\mu_{FeNNV_0} = 1.16$ and 2.1, which is compatible with iron going from a d$^3$-occupancy (Fe$^{3+}$) to d$^4$ (Fe$^{2+}$). This change in iron d-occupancy is unfavorable and has been suggested previously to cause the high $E_f$ in LaFeO$_3$. A thorough discussion on V$_0$ formation in SmCoO$_3$ has been presented in a previous publication\cite{48} and is thus only briefly mentioned here.

### 3.4 Thermal expansion coefficient (TEC)

The TECs of traditional electrolyte materials are in the region of $\sim 10$–$13 \times 10^{-6}$ K$^{-1}$ and SmCoO$_3$ has a calculated TEC of 17.7 $\times 10^{-6}$ K$^{-1}$. These high TECs are commonplace for cobalt perovskites, and they are known to increase with Sm-site doping, as this increases oxygen deficiency in the lattice, leading to further lattice volume expansion upon heating. Co-site doping can decrease TEC, as seen in Fig. 6 and Table S8 (ESI), which would make the materials more practical as SOFC cathodes, making the electrolyte and cathode compatible. Encouragingly, most systems investigated here do show lowered TEC compared to SmCoO$_3$, although none are directly in the range of common SOFC electrolytes. As such, none of the materials are suitable as SOFC cathodes in their current compositions. Mn-doping is seen to decrease TEC the most, but it also varies greatly with $x$. On the other hand, Fe-doping barely affects the TEC at any $x$. Doping with copper shows no significant change in TEC at low $x$, but it increases for $x = 0.5$. Finally, Ni-doping shows similar behaviour to Mn-doping, but does not reduce TEC as readily. Although these results are generally positive in terms of lowering TEC, they are not sufficient to match an acceptable TEC range.

### 4. Conclusion

In this paper we have presented a detailed atomic-level computational study of Sm$_x$Co$_{1-x}$O$_3$ materials, where B = Fe, Mn, Ni, and Cu, and $x = 0.125, 0.25, 0.5, 0.75$ and 1.00. After a complete study of the dopant configurations, the most stable dopant distributions and concentrations were determined, from which the electronic and magnetic properties, hole formation, oxygen vacancy formation energies, and thermal expansion coefficients were calculated.

Regardless of the dopant, doping on the Co-site induces a distortion of the Co–O bond that forces different Co d-orbital occupations. This effect, in combination with the d-orbital occupation of the dopants, explains why the majority of the systems become ferromagnetic, with the exception of SmCu$_{0.25}$Co$_{0.75}$O$_3$ and SmCu$_{0.75}$Co$_{0.25}$O$_3$. The overlap between the $e_g$-orbitals of the dopant and cobalt around the Fermi level explains the impressively high electrical conductivity found for SmMn$_{0.125}$Co$_{0.875}$O$_3$ compared to SmFe$_{0.125}$Co$_{0.875}$O$_3$, where the presence of an electronic band explains the insignificant
calculated electronic conductivity. We have also illustrated that doping with Cu and Ni does not significantly improve the electronic conductivity of the perovskite. Hence, only Mn-doping would be beneficial for this material as an SOFC cathode, as electronic conductivity is of vital importance for intermediate temperature SOFC cathodes.

Furthermore, B-site doping was not found to reduce significantly the oxygen vacancy formation energy when B = Mn or Fe, but it does decrease with B = Cu or Ni. In general, the most common V₀ configuration was found to be Co–V₀–Co, with the reduction of cobalt. Finally, TECs were calculated, where Mn-doping showed the largest decrease at low x. Thus, from the results obtained from the combination of our DFT calculations and MD simulations, we conclude that SmMnxCo2−xO3 at x = 0.125 or x = 0.25 would be the most favorable composition to improve SmCoO3 as an IT-SOFC cathode material, but that doping with Fe would be disadvantageous due to the low electronic conductivity. However, to realize the potential of doped SmCoO3 as a SOFC cathode material, studies would need to be conducted combining both the Co-site doping studied here with Sm-doping.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge the Engineering and Physical Sciences Research Council (EPSRC) for financial support (Grants references EP/K016288/1 and EP/K001329/1). We also acknowledge the use of the UCL Legion High Performance Computing Facility (Legion@UCL) and the UCL Grace High Performance Computing Facility (Grace@UCL), and associated support services, in the completion of this work. Finally, via our membership of the UK’s HPC Materials Chemistry Consortium, which is funded by EPSRC (EP/L000202), this work made use of the facilities of ARCHER, the UK’s national high-performance computing service, which is funded by the Office of Science and Technology through EPSRC’s High End Computing Programme. DL_POLY_4 has been obtained from STFC’s Daresbury Laboratory via the website http://www.ccp5.ac.uk/DL_POLY. We acknowledge use of STFC Hartree Centre resources in this work. The STFC Hartree Centre is a research collaboratory in association with IBM providing High Performance Computing platforms funded by the UK’s investment in e-Infrastructure. E. O. gratefully acknowledges EPSRC funding from the UCL Centre for Doctoral Training in Molecular Modelling and Materials Science (EP/G036675/1).

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