FIRST PRINCIPLES CALCULATIONS OF OXYGEN VACANCY FORMATION AND MIGRATION IN MIXED CONDUCTING $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ PEROVSKITES

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Abstract

First-principles supercell calculations of oxygen vacancies in the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (BSCF) perovskites are presented. We analyze the dependences of the defect (oxygen vacancy) formation and migration energies on the Fe content and compare the calculated properties with those of related $\text{LaCoO}_3$ and $\text{LaFeO}_3$ perovskites.

1. Introduction

Mixed conducting perovskites have been used as cathode materials in solid oxide fuel cells (SOFC) since early 1980s, and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) was the first widely applied oxide cathode material. Currently, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_{3-\delta}$ (BSCF) shows the best oxygen exchange performance [1,2]. Despite of having drawbacks for application as a SOFC cathode (e.g. reactivity with electrolyte materials, $\text{CO}_2$ poisoning and a phase transformation at $T < 900$ °C, see [3] and references therein), it is still a promising material for oxygen permeation membranes [4]. As it is well understood by now [3,5], both the high oxygen vacancy concentration at the cathode surface and high vacancy mobility are key factors for the fast oxygen reduction at SOFC cathodes and at the surface of permeation membranes. While bulk oxygen vacancy concentrations and mobilities are available from experiments, the respective quantities for the surface layer, which are decisive for the surface reaction, are almost impossible to be measured. Hence, an extensive set of large-scale first principles DFT calculations was carried out for $\text{LaMnO}_3$ and LSM [6,7,8,9]. The first ab initio study for
complex BSCF perovskites has been performed only recently [10]. Here, we analyze the atomic and electronic structure of bulk oxygen vacancies, their formation and migration energies, and how these properties depend on the chemical composition of the BSCF perovskite.

2. Computational details
We employed the *ab initio* DFT computer code VASP 4.6 in conjunction with the projector-augmented method (PAW) and plane wave basis set [11]. The exchange-correlation GGA functional was of PBE-type. In the library of potentials supplied with the VASP code there are a single PAW PBE potential for Ba, Sr and Co and several potentials for Fe and O, which differ by the number of valence electrons and the basis set cut-off energy, respectively. Test calculations showed that there is practically no dependence of the lattice constant (< 0.05 %) as well as the binding energy (< 0.4 %) of BSCF upon the choice of Fe PAW PBE potentials, thus we used the Fe \((3d^74s^1)\) and Co \((3d^84s^1)\) potentials. For oxygen, we used the *soft* PAW PBE potential, which gives an O\(_2\) molecule binding energy very close to the experimental values and a reasonable bond length (5.24 eV and 1.29 Å, cf. experimental 5.12 eV and 1.21 Å [12]). The 4x4x4 k-point mesh in the Brillouin zone was created by the Monkhorst-Pack scheme [13] for the Ba\(_4\)Sr\(_4\)Co\(_8\)Fe\(_{8y}\)O\(_{24}\) supercells. Ion charges were calculated by the Bader method [14]. The kinetic energy cut-off for the plane wave basis set is to 520 eV. Basic properties of defect-free BSCF are discussed in ref. [10]. The spin states of Fe, Co ions are obtained self-consistently from the calculations. Here, we use 40-atom supercells (cubic \(ABO_3\) unit cell expanded twice along all three translation vectors) with oxygen vacancies \((V_o)\). We calculate several cation arrangements in Ba\(_{0.5}\)Sr\(_{0.5}\)Co\(_{1-y}\)Fe\(_y\)O\(_{3-\delta}\) (Ba and Sr are placed in a regularly alternating arrangement) with varying Fe concentration \(0 \leq y \leq 1\). Typical structures are shown in Fig. 1 along with different positions and surroundings of oxygen vacancies. These structures remain cubic, and we optimised all atomic positions in the supercells. For Ba\(_{0.5}\)Sr\(_{0.5}\)Co\(_{0.75}\)Fe\(_{0.25}\)O\(_{3-\delta}\) we exemplarily compared the energies for relaxed and fixed lattice parameters; they differ typically no more than 0.05 eV. All data given in this paper refer to the lattice parameter being fixed at the value of the respective \(\delta = 0\) material.
3. Results and discussion

We start with calculations for Ba$_{0.5}$Sr$_{0.5}$Co$_{0.75}$Fe$_{0.25}$O$_3$ without O deficiency. The optimized lattice constant is 3.902 Å. From the calculations, iron is found to be in the high spin state (Fe$^{4+}$: $t_{2g}^3 e_g^1$, Fe$^{3+}$: $t_{2g}^3 e_g^2$), and Co in intermediate spin state (Co$^{4+}$: $t_{2g}^4 e_g^1$, Co$^{3+}$: $t_{2g}^5 e_g^1$). The Bader (topological) atomic charges indicate a considerable covalent contribution in the Co-O and Fe-O bonds: Co $+1.61$ e$_0$, Fe $+1.66$ e$_0$, O $-1.07$ e$_0$, whereas Ba and Sr charges are closer to the formal ones ($+1.59$ e$_0$ and $+1.62$ e$_0$). Fig. 2 shows the projected electronic densities of states (DOS). For the same $\delta$ but different $V_O$ locations (Co $V_O$ Co versus Co $V_O$ Fe) the DOS look very similar (thus only the Co $V_O$ Co configuration is depicted), which emphasizes a significant degree of electron delocalization.

Since the computational method generates absolute energies for each particular system which are hard to compare due to the difference in stoichiometries, the energy scale is aligned such that the O2$s$ core states coincide (this also yields a good coincidence of the O2$p$ states). The electrons left behind upon oxygen removal force the Fermi energy $E_F$ upward. The shift is 0.17 eV / 0.42 eV for Ba$_{0.5}$Sr$_{0.5}$Co$_{0.75}$Fe$_{0.25}$O$_{3-\delta}$ ($\delta = 0.125 / 0.375$), and stronger - by 0.25 eV / 0.60 eV - for Ba$_{0.5}$Sr$_{0.5}$FeO$_{3-\delta}$, which could be understood from the DOS close to $E_F$. The Fe DOS is very small close to $E_F$ and exhibits a gap of $\approx 2$ eV. In contrast, the Co DOS directly above $E_F$ is much larger, thus the electron allocation upon the oxygen removal requires a smaller increase of $E_F$. 

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{Fe and Co arrangements in Ba$_{0.5}$Sr$_{0.5}$Co$_{1-y}$Fe$_y$O$_3$ in the 2x2x2 supercell (Ba and Sr not shown for clarity; for $y > 0.5$ Fe and Co have to be interchanged). Oxygen vacancy positions are indicated by numbers (see Table 1, only one of equivalent $V_O$ configurations is shown). X: vacancy configuration for $\delta = 3/8$ (3 $V_O$ per supercell), Y: exemplary configuration for $\delta = 0.5$.}
\end{figure}
Figure 2: Projected Co, Fe and O density of states of a) \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_{3-\delta} \) and b) \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta} \) for various \( \delta \). The energy scale is adjusted to align the O2s states (solid vertical line), dashed lines indicate the relevant Fermi energies.

These characteristic differences of Fe and Co DOS are also consistent with the experimental finding of a significantly lower electronic conductivity for Fe-rich materials compared to Co-rich compositions [15,16], and with the observation of a "Fe\(^{3+}\) plateau" in LSF [17] while Co smoothly changes the oxidation state from 4+ through 3+ to 2+ in related LSC perovskites [18]. A comparison with qualitative BSCF and LSCF band schemes deduced from defect
chemical studies reveals that they correctly cover some key features (the narrow empty Fe band above empty Co states [23]; considerable fraction of empty Co DOS directly above $E_F$ [26]) but are less reliable for other aspects (extension of O 2$p$ states above $E_F$ [26]).

3.1. Defect formation energies

![Figure 3: Oxygen vacancy formation energy $E_V$ as function of iron content $y$ in Ba$_{0.5}$Sr$_{0.5}$Co$_{1-y}$Fe$_y$O$_{2.875}$ (fixed lattice parameter, see text below).](image)

The bulk oxygen vacancy formation energies, $E_V$, for Ba$_{0.5}$Sr$_{0.5}$Co$_{1-y}$Fe$_y$O$_{2.875}$ as final states are shown in Fig. 3 and Table 1: $E_V$ increases with Fe content almost linearly from $\approx$ 1.2 eV up to 2.2 eV. The similar $E_V$ values of different local vacancy configurations (Co$_V$O$\_-$Fe and Co$_V$O$\_-$Co, Fe$_V$O$\_-$Fe) but same iron content and $\delta$ reflect the delocalized character of the electronic density. The increase of $E_V$ with increasing Fe content can be related to the DOS and the stronger increase of the Fermi energy for Fe-rich materials.

The calculated vacancy formation energies for BSCF (formally reducing (Fe,Co)$^{4+}$ to (Fe,Co)$^{3+}$) are smaller than for SrTiO$_3$ (ca. 6 eV, formally Ti$^{4+}$ → Ti$^{3+}$ [19]) and La$_{0.75}$Sr$_{0.25}$MnO$_3$ (2.7 eV, formally Mn$^{4+}$ → Mn$^{3+}$ [9,20]), in particular for Co-rich materials owing to the easy reduction of Co ions. The trend that cobalt-rich systems exhibit a lower $E_V$ is in qualitative agreement with the fact that the vacancy concentration - for given temperature and oxygen partial pressure - increases from Ba$_{0.5}$Sr$_{0.5}$FeO$_{3-\delta}$ to Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ [3,21,22] (for higher Co content the cubic perovskite structure is unstable), as well as from La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ and La$_{0.6}$Sr$_{0.4}$Co$_{0.6}$Fe$_{0.4}$O$_{3-\delta}$ [23]. Comparing the calculated $E_V$ to experimental data we have to account for the much higher vacancy concentrations in the real samples.

While the vacancy formation energy in Ba$_{0.5}$Sr$_{0.5}$FeO$_{3-\delta}$ shows only a small variation with
oxygen deficiency $\delta$, the dependence is very strong in $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ [24]. Extrapolating these experimental data to low vacancy concentrations, the same trend is obtained as in the DFT calculations, i.e. lower $E_V$ values for Co-rich compositions, although the absolute $E_V$ values differ.

**Table 1:** Oxygen vacancy formation energies $E_V$ (with respect to $1/2$ free O$_2$ molecule in triplet state, 5.24 eV) for selected $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-y}\text{Fe}_y\text{O}_{2.875}$ compositions, change of ion charge $\Delta q$ for neighbouring Co, Fe, O (in second coordination sphere); and vacancy migration barriers $E_m$ (initial state = column 2, final state indicated in last column). For definition of cation and vacancy configurations see Fig. 1.

<table>
<thead>
<tr>
<th>$y$</th>
<th>cation and vacancy configuration</th>
<th>$E_V$/ eV</th>
<th>$\Delta q_{Co}$/ e$_0$</th>
<th>$\Delta q_{Fe}$/ e$_0$</th>
<th>$\Delta q_{O}$/ e$_0$</th>
<th>$E_m$/ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$\text{CoV}_0\text{Co}$</td>
<td>1.21</td>
<td>2'(-0.13)</td>
<td>-</td>
<td>8'(-0.06)</td>
<td>0.40</td>
</tr>
<tr>
<td>0.25</td>
<td>B2 $\text{CoV}_0\text{Co}$</td>
<td>1.34</td>
<td>2'(-0.12)</td>
<td>-</td>
<td>8'(-0.06)</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>B1 $\text{CoV}_0\text{Fe}$</td>
<td>1.40</td>
<td>-26</td>
<td>-0.11</td>
<td>8'(-0.06)</td>
<td>0.46</td>
</tr>
<tr>
<td>0.5</td>
<td>C1 $\text{CoV}_0\text{Fe}$</td>
<td>1.63</td>
<td>-0.11</td>
<td>-0.11</td>
<td>8'(-0.06)</td>
<td>-</td>
</tr>
<tr>
<td>0.75</td>
<td>B1 $\text{CoV}_0\text{Fe}$</td>
<td>1.92</td>
<td>-0.11</td>
<td>-0.10</td>
<td>8'(-0.06)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>B2 $\text{FeV}_0\text{Fe}$</td>
<td>1.82</td>
<td>-</td>
<td>2'(-0.12)</td>
<td>8'(-0.06)</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>$\text{FeV}_0\text{Fe}$</td>
<td>2.22</td>
<td>-</td>
<td>2'(-0.13)</td>
<td>8'(-0.05)</td>
<td>0.72</td>
</tr>
</tbody>
</table>

The charge redistribution (column 4 in Table 1) shows that when an O atom is removed, the largest part of its negative charge is distributed over the nearest transition metal ions in the first coordination sphere, whereas the eight oxygen atoms in the second coordination sphere receive $\approx 0.06$ e$_0$ each. That is, $\approx 0.7$ e$_0$ are localized on ions surrounding the $\text{V}_0$. Depending on the actual cation and vacancy configuration and on the region of averaging (only Fe/Co directly neighboring the $\text{V}_0$, or whole supercell), either Fe or Co receive the larger share of the transferred electrons. This is in qualitative agreement with in-situ XAS experiments, indicating that it depends delicately on $T$, $p\text{O}_2$ which of the transition metals (or even the oxygen ions) experiences the larger electron transfer [26]. The absolute effective charge is generally smaller for Co, e.g. $q_{Co} = +1.61$ e$_0$ and $q_{Fe} = +1.66$ e$_0$ in $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_3$, in qualitative agreement with EELS results for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ [25] and XAS on $\text{Ba}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ [26].
Figure 4: Oxygen vacancy formation energy $E_V$ as function of oxygen deficiency $\delta$ in $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_{3-\delta}$ (solid symbols; for $\delta \geq 0.5$ •••• denotes a combination of Co-$V_O$-Co and Co-$V_O$-Fe) and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ (open symbols).

Fig. 4 shows the calculated vacancy formation energies for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_{3-\delta}$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$. The vacancy formation energies in Fig. 4 increase approximately linearly with vacancy concentration. This holds even for $\delta > 0.5$ (i.e. for the average Fe and Co oxidation state decreasing below 3+) for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_{3-\delta}$, in accord with the experimental data showing no phase transition or discontinuity in other properties. While an increase of the oxidation enthalpy with increasing $\delta$ is found experimentally [24], the more pronounced increase for the cobalt-rich materials is not obtained in the present calculations. This might be related to Co$^{3+}$ disproportionation occurring at elevated temperatures which is neglected in the DFT calculations performed for 0 K [27].

Fig. 4 also indicates that a simple defect-chemical model (a single mass action law) for $\text{Ba}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ will not be applicable. Since even for fixed cation composition, $E_V$ varies strongly with $V_O$ concentration, a single mass-action law cannot be expected to correctly reproduce the vacancy formation reaction. Instead, elastic and electrostatic defect interactions as well as the energy distribution of Co and Fe states and the involvement of the oxygen states in the redox reaction to varying degree [26] would have to be included.
3.2. Defect migration energies

Figure 5: Variation of oxygen vacancy migration barrier \( E_m \) in \( Ba_{0.5}Sr_{0.5}Co_{1-y}Fe_yO_{2.875} \) with Fe fraction \( y \) and number of surrounding Fe ions.

Anion migration occurs by a jump of an oxygen ion into a \( V_O \) along the edge of the \( BO_6 \) octahedron on a path slightly curved away from the \( B \) cation (nevertheless, the \( B-O \) distance in the transition state is shorter than in the initial state). In the transition state, the migrating oxygen ion passes through a triangle set up by two \( A \)- and one \( B \)-cations. Table 1 summarizes the bulk \( V_O \) migration barriers for \( Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{2.875} \) (for "asymmetric" jumps, e.g. between \( CoV_OCo \) and \( CoV_OFe \) configurations, the difference in the forward and backward barrier corresponds to the difference in the respective \( E_V \), typically \( \leq 0.1 \) eV).

The DFT-derived \( V_O \) migration barriers in \( LaMnO_{3-\delta} \) [6], \( LaFeO_{3-\delta} \) and \( LaCoO_{3-\delta} \) [28] perovskites all amount to \( 0.8-0.9 \) eV; this is in good agreement with the essentially materials-independent vacancy diffusion coefficient in \( (La,Sr)(Mn,Fe,Co)O_{3-\delta} \) perovskites [29,30]. In contrast, Fig. 5 shows a strong variation within the \( Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{2.875} \) family with the migration barriers \( E_m \) ranging from 0.4 eV to over 0.7 eV. A pronounced, roughly linear increase is found if the barrier is plotted either versus the sum of direct Fe neighbours of the \( V_O \) in the initial and final state (a local property), or Fe content (a long-range averaged quantity, giving a slightly better correlation), indicating that both short- and long-range environments affect \( E_m \). The migration barriers fall into the same range as obtained from experimental vacancy diffusion coefficients for \( Ba_{0.5}Sr_{0.5}Co_{0.3}Fe_{0.2}O_{3-\delta} \) (0.5 eV), \( Ba_{0.5}Sr_{0.5}FeO_{3-\delta} \) and \( SrFeO_{3-\delta} \) (0.9 eV) [3,31]. While the concept of the "critical radius \( r_c \)" [32]
is useful for perovskites with a Goldschmidt tolerance factor \( t < 1 \), an estimate of \( r_c \) based on ionic radii yields smaller values for \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta} \) than for \( \text{LaFeO}_{3-\delta} \) and \( \text{LaCoO}_{3-\delta} \), i.e. \( V_0 \) migration should be more energetically costly in BSCF.

One reason for this wrong prediction, which is based on the cation geometry while the oxygen ion is still in the initial state, can be seen from Table 2 by looking at the displacements within the triangle of two \( A \)-site and one \( B \)-site cations through which the O jumps. For both materials the \( A1-A2 \) distance increases by \( \approx 0.2 \) Å, but in BSCF the displacement of the \( B \) cation away from the migrating O is three times larger than in \( \text{LaCo}_{1-x}\text{Fe}_x\text{O}_{3-\delta} \), which is possible due to \( t > 1 \) (i.e. in a perovskite where the \( B \) cation is "too small"). Together with the higher polarizability in particular of \( \text{Ba}^{2+} \), this higher flexibility of the lattice seems to decrease migration barrier. The increase of \( E_m \) with Fe content for \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta} \) may be related to the \( A1-A2-B \) triangle in the transition state having almost the same size for BSC and BSF (Table 2), but Fe (high spin state) being larger than Co (intermediate spin) decreases the available open space for the migrating O. Since the (Co,Fe)-O distance is shorter in BSCF compared to \( \text{LaCo}_{1-x}\text{Fe}_x\text{O}_{3-\delta} \), this size difference (and maybe also a higher polarizability of Co compared to Fe) seems to affect \( E_m \) in BSCF while it appears to be less important in \( \text{LaCo}_{1-x}\text{Fe}_x\text{O}_{3-\delta} \).

In principle, also a reduction of the oxygen ion charge in the transition state (decreasing its effective ion size) could affect the migration barriers, but such a charge redistribution was found to be small in \( \text{LaNiO}_{4+\delta} \) [33]. In contrast to our DFT calculations, the increased \( V_0 \) mobility in BSC compared to BSF (agreeing well with higher diffusion coefficients for \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta} \) than for \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta} \) [3,31]) is not reproduced in semi-empirical pair-potential molecular dynamics simulations [34], yielding similar diffusivities for \( \text{Ba}_{0.8}\text{Sr}_{0.2}\text{CoO}_{2.5} \) and \( \text{Ba}_{0.8}\text{Sr}_{0.2}\text{FeO}_{2.5} \).

**Table 2:** Distances (in Å) in the transition state between the migrating O and cations, and between the corners of the \( A1-A2-B \) cation triangle. Italic numbers give the change (in Å) relative to the initial state; the last column gives the outward displacement of the \( B \) cation away from the migrating O. BSF = \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_3 \), BSC = \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 \).

<table>
<thead>
<tr>
<th>lattice constant</th>
<th>O to ( A1 = ) La or Ba</th>
<th>O to ( A2 = ) La or Sr</th>
<th>O to ( B = ) Co or Fe</th>
<th>( A1-A2 )</th>
<th>( A1-B )</th>
<th>( A2-B )</th>
<th>( B ) displacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{LaFeO}_3 )</td>
<td>3.88</td>
<td>2.26</td>
<td>2.26</td>
<td>1.84 -0.10</td>
<td>4.14 +0.26</td>
<td>3.44</td>
<td>3.44 +0.04</td>
</tr>
<tr>
<td>( \text{LaCoO}_3 )</td>
<td>3.83</td>
<td>2.28</td>
<td>2.28</td>
<td>1.78 -0.13</td>
<td>4.05 +0.22</td>
<td>3.48</td>
<td>3.48 +0.06</td>
</tr>
<tr>
<td>BSF</td>
<td>3.92</td>
<td>2.57</td>
<td>2.40</td>
<td>1.68 -0.28</td>
<td>4.14 +0.22</td>
<td>3.56</td>
<td>3.78 +0.14</td>
</tr>
</tbody>
</table>
4. Conclusions
The trends in vacancy formation energy $E_V$ and migration barriers in $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ obtained from our DFT calculations are in good agreement with experimental data as far as available, although the absolute $E_V$ values are moderately overestimated. The gradual increase of $E_V$ with increasing iron content and also with increasing oxygen deficiency can be rationalized based on the calculated electronic density of states with unoccupied iron states located higher in energy than cobalt states (and having a smaller band width). For the calculated low oxygen vacancy migration barriers in BSCF, the fact that Ba-containing materials allow for larger $B$ cation displacements in the transition state appears to be important. Our calculation confirm that the compositions with the highest cobalt content which still form the cubic perovskite phase (i.e. Fe content $y \approx 0.2$) are most suitable for oxygen permeation membranes since they combine the lowest vacancy formation energy $E_V$ with the lowest $V_{O}$ migration barrier $E_m$. Further detailed analysis of the lattice polarization effects in defect formation and migration is in progress.

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References
Please note that since overlap between the transition metal and oxygen orbitals is required for electronic conductivity, the nonzero density of Co states at $E_F$ does not necessarily imply metallic conductivity.


It is important to choose the same change of the formal oxidation states for a proper comparison of vacancy formation energies: while $E_V = 2.7$ eV for (Mn$^{4+}$ → Mn$^{3+}$) for La$_{0.75}$Sr$_{0.25}$MnO$_3$, $E_V$ amounts to more than 4 eV in LaMnO$_3$ where Mn$^{3+}$ → Mn$^{2+}$ [8]. For the inverse reaction (oxidation) one has to consider if it is formulated for O$_2$ or 1/2 O$_2$.


For the interpretation of experimental data for La$_{0.4}$Sr$_{0.6}$CoO$_{3-\delta}$ measured at 800 °C a slightly endothermic disproportionation 2 Co$^{3+}$ $\rightarrow$ Co$^{2+}$ + Co$^{4+}$ is discussed, see e.g. E. Bucher, W. Sitte, G.B. Caraman, V.A. Cherepanov, T.V. Aksenova, M.V. Ananyev, Solid State Ionics 177 (2006) 3109.

Y.A. Mastrikov, unpublished.


$r_c$ is the radius of the largest empty circle that can be inscribed into the triangle of the B and the two A cations surrounding the oxide ion in the transition state. A larger $r_c$ should facilitate the oxide ion jump, see J.A. Kilner, R.J. Brook, Solid State Ionics 6 (1982) 237.
