Atomistic study of dopant site-selectivity and defect association in the lanthanum gallate perovskite

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Advanced modelling techniques have been used to investigate the defect properties of the LaGaO₃ ionic conductor on the atomic-scale. The present study addresses a variety of topics, but focuses on the site-selectivity of a wide range of dopants, the influence of A-site deficiency, the nature of dopant–vacancy association, and the energetics of oxidation in the transition-metal doped oxide. Ion size trends are found for selectivity of a wide range of dopants, the influence of A-site deficiency, the nature of dopant–vacancy compensation. Dopant–vacancy clusters for a wide range of dopant ions have been examined. A minimum in the binding energy occurs for Sr⁺² on La³⁺, which would be beneficial to oxygen ion conductivity. Dopant–vacancy association for isovalent (M⁵⁺) substitution indicates elastic strain effects. We have considered complex clusters (xMgO₃•yV'O) of x up to 12 within 2D and 3D structures, which may be related to possible “nano-domain” formation at higher dopant regimes. Favourable oxidation on energetic grounds is found for Ni⁺² and Cu⁺² doping, suggesting p-type conductivity at increasing oxygen partial pressures.

1. Introduction

Oxygen ion transport in ceramic oxide materials has attracted considerable interest due to the promising electrochemical applications such as solid oxide fuel cells (SOFCs), oxygen separation membranes and partial oxidation reactors. In this field, high oxygen ion conductivity has been reported in the LaGaO₃-based perovskite,¹,² which is superior to that found in the conventional Y₂Zr₂O₇ electrolyte at lower temperatures. It is apparent that a significant decrease in the SOFC operating temperature would be an important practical advance. The incorporation of cation dopants to form the system Lax₁₋yxSr₁₋yGa₁₋xMgₓO₃₋δ (often termed LSGM), gives rise to the highly mobile oxygen vacancies that are responsible for the observed ionic conductivity.

Following the initial discovery by Ishihara et al.,¹,² numerous experimental studies have been carried out on the LaGaO₃-based (LSGM) material, which include reports covering oxygen ion conductivity,³–¹³ structural properties,¹⁴–²³ electrolyte performance within SOFCs²⁴–²⁷ and the effect of transition-metal doping.²⁸–³⁶ Such doping with multivalent transition-metal cations in order to introduce electronic conductivity is of interest for developing applications of mixed conductors (e.g. SOFC electrodes, hydrocarbon oxidation reactors). Other perovskite oxides such as (La, Sr)MnO₃ and (La, Sr)(Co, Fe)O₃ are already known to exhibit either mixed or electronic conductivities. More recently, there have been a few studies of cation diffusion⁷–⁹ (including creep behaviour) and of cation non-stoichiometry in LSGM.⁴⁰ It is apparent that variations in the A/B cation ratio of ABO₃ perovskites can have a significant affect on their properties.

However, despite the investigations referred to above, there is only limited information on the fundamental microscopic factors that control the macroscopic properties, such as lattice defects, dopant-site selectivity and redox processes. Furthermore, there is conflicting debate as to the extent and nature of the association between dopant ions and oxygen vacancies.

This detailed study attempts to provide further insight into these problems by using atomistic simulation techniques, which are now well established tools in solid state chemistry. The reliability of such an approach has been demonstrated by our simulation studies of defects, ion transport and surface structures of other perovskite oxides (e.g. LaMnO₃, LaCoO₃).⁴¹–⁴⁴

Results from our earlier investigation of the LaGaO₃ system⁴⁵ indicate that oxygen vacancy migration follows a curved pathway in which the saddle-point of the migrating oxygen ion sits just outside the edge of the GaO₆ octahedron and away from the adjacent Ga ion (leading to a calculated activation energy of 0.73 eV). This study also finds that Sr⁺² on La³⁺ and Mg⁺² on Ga³⁺ are the most favourable acceptor dopants on energetic grounds. A recent neutron scattering study²³ of doped LaGaO₃ provides evidence for our predicted curved pathway.

De Souza⁴⁶ has also employed simulation methods to investigate impurity incorporation and, in particular, cation defect migration in LaGaO₃.

The present study builds and extends upon this earlier work by turning attention to the site-selectivity of a wider range of dopants (including Co, Fe, Ni, Mn, In, Nb), the influence of A/B cation non-stoichiometry, the nature of dopant–vacancy association, and the energetics of oxidation.

2. Simulation techniques

The computational techniques used in this work are well established and have been reviewed in detail elsewhere.⁴⁷ Hence, only a brief summary is given here.

The calculations are based upon the Born model of ionic solids with ions assigned integral charges corresponding to their formal oxidation states. The interactions between the ions are formulated in terms of long-range Coulombic forces and short-range forces that account for electron cloud overlap (Pauli repulsion) and dispersion (van der Waals) interactions. The short-range interactions are modelled with a Buckingham potential of the form:

\[ V(r) = A_{ij} \exp(-r/r_0) - C_{ij}/r^6 \]  

(1)
where $A_{ij}$, $p_{ij}$, and $C_{ij}$ are the potential parameters. Because charge defects will polarize other ions in the lattice, ionic polarizability must be incorporated into the potential model. The shell model provides a simple description of such effects and has proven to be effective in simulating the dielectric properties of ceramic oxides. An important feature of these calculations is the treatment of lattice relaxation about the point defect or migrating ion. The Mott–Littleton approach is to partition the crystal lattice into two regions so that ions in a spherical inner region surrounding the defect are relaxed explicitly. In contrast, the remainder of the crystal, where the defect forces are relatively weak, is treated by more approximate quasi-continuum methods. In this way, local relaxation is effectively modelled and the crystal is not considered simply as a rigid lattice through which ion species diffuse.

The potential parameters for LaGaO$_3$ are exactly the same as in our previous study,$^{45}$ which were derived by empirical procedures using the observed orthorhombic perovskite structure.$^{48}$ This structure is built upon a framework of corner-linked GaO$_6$ octahedra; the orthorhombic phase can be considered as due purely to tilts of these octahedra from the ideal cubic configuration. The potentials for the La–O and O–O interactions were transferred directly from the analogous simulation study of the LaMO$_3$ (M = Cr, Mn, Fe, Co) perovskites.$^{43}$ We note that the interatomic potentials for the dopant ions are exactly those of the corresponding binary metal oxides$^{49}$ that have been applied to analogous studies of the LaMO$_3$ perovskites.$^{41,43}$

Energy minimisation methods identify the static configuration of lowest energy and are essentially ‘zero Kelvin’ calculations, with no representation of thermal effects. It is possible to add a treatment of the vibrational properties of the system via the quasi-harmonic approximation as discussed by Catlow.$^{57}$ Despite these features, minimisation techniques have been readily applied to materials with large complex unit cells and have been used to refine approximate crystal structures. In essence, the empirical interatomic potentials are derived within the context of a room temperature or higher temperature experimental structure.

Before carrying out defect calculations, the crystal structure of LaGaO$_3$ was simulated using energy minimisation procedures. The calculated bond distances and lattice parameters are compared with experimental values in Table 1. Examination of the differences shows good agreement between experimental and simulated structures, as well as reasonable accord with the measured dielectric constant.$^{50}$ These results provide support for the validity of our potential model for the subsequent defect simulations.

### Table 1  Calculated and experimental structural parameters of orthorhombic LaGaO$_3$

<table>
<thead>
<tr>
<th>Property</th>
<th>Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit cell parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a [Å]</td>
<td>5.485</td>
<td>5.527</td>
</tr>
<tr>
<td>b [Å]</td>
<td>7.752</td>
<td>7.781</td>
</tr>
<tr>
<td>c [Å]</td>
<td>5.481</td>
<td>5.496</td>
</tr>
<tr>
<td>$\alpha = \beta = \gamma$ (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Bond distances [Å]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La–O(1)</td>
<td>2.538</td>
<td>2.418</td>
</tr>
<tr>
<td>La–O(2)</td>
<td>2.541</td>
<td>2.400</td>
</tr>
<tr>
<td>Ga–O(1)</td>
<td>1.958</td>
<td>1.977</td>
</tr>
<tr>
<td>Ga–O(2)</td>
<td>1.960</td>
<td>1.956</td>
</tr>
<tr>
<td>Lattice energy [eV]</td>
<td>-143.250</td>
<td></td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>16.79</td>
<td>$\sim 25^\circ$</td>
</tr>
</tbody>
</table>

$^\dagger$ Dube et al.$^{50}$

### Fig. 1  Calculated solution energies as a function of ion radius for divalent (M$^{2+}$) dopants at both La and Ga sites in LaGaO$_3$. (The lines are guides to the eye.)

#### 3. Results and discussion

##### 3.1. Dopant substitution in LaGaO$_3$

In terms of modes of “solution” into the LaGaO$_3$ material, dopant ions can substitute at either La$^{3+}$ or Ga$^{3+}$ sites with the creation of charge-compensating defects. This raises key questions in relation to the favoured substitution site, the type of compensating defect and the influence, if any, of A and B site cation size. Our simulation methods can probe these issues by generating quantitative estimates of the relative energies of different modes of solution. Although the prediction of the precise amount of dopant that can be incorporated is less straightforward, our results can provide a useful systematic guide to the site-selectivity for different dopant species and to trends in dopant solubility. Such an approach has been applied successfully to a variety of oxides.$^{41,51,52}$

We have therefore examined a wide range of dopants in LaGaO$_3$ including divalent (e.g. Sr$^{2+}$, Ni$^{2+}$, Cu$^{2+}$), trivalent (e.g. Co$^{3+}$, Fe$^{3+}$, Mn$^{3+}$, In$^{3+}$), tetravalent (e.g. Ti$^{4+}$, Zr$^{4+}$, Th$^{4+}$) and pentavalent (e.g. Nb$^{5+}$, Ta$^{5+}$) ions. The results are discussed in the following sub-sections.

#### 3.1.1 M$^{2+}$ substitution

Divalent dopants (as MO oxides) can substitute at either La$^{3+}$ or Ga$^{3+}$ sites with the creation of oxygen vacancies; such “acceptor” doping can be represented by the following defect reactions:

La-site: \[ \text{MO} + \frac{1}{2} \text{O}_2^\cdot \rightarrow \text{M}^{2+} + \frac{1}{2} \text{La}_2\text{O}_3 \] (2)

Gasite: \[ \text{MO} + \text{Ga}^{3+} + \frac{1}{2} \text{O}_2^\cdot \rightarrow \text{M}^{2+} + \text{Ga}_2\text{O}_3 \] (3)

where, in Kröger–Vink notation,$^{53}$ $\text{M}^{2+}$ signifies a dopant substitutional and $\text{V}_\text{O}^\cdot$ an oxygen vacancy. The energies of these “solution” reactions can be evaluated by the simulation methods by combining appropriate defect and lattice energy terms. The resulting solution energies for a series of alkaline-earth and divalent transition-metal dopants in LaGaO$_3$ are presented as a function of ion size in Fig. 1. We note that the dopant radii for six-coordination from Shannon$^{54}$ are used...
since 12-coordination values are not available for all the ions considered. In any case, our main concern here is to examine the trend in energetics between substitution at the La and Ga sites.

Examination of the results (Fig. 1) reveals three main points. First, low favourable solution energies are found for Sr$^{3+}$ at the La site and Mg$^{2+}$ at the Ga site, in accord with conductivity studies and with recent calorimetry measurements. There are clear correlations with dopant size with unfavourable values for substitution of the large Ba$^{2+}$ in line with the observed low solubility. These results provide support for the validity of our simulation approach and are compatible with previous calculations.

Second, the transition-metal dopants, Co$^{2+}$, Ni$^{2+}$ and Cu$^{2+}$ are predicted to occupy the Ga site, as expected. However, the precise oxidation state of the Co dopant is still unclear from experiment. As noted previously, we find a low solution energy for Cu$^{2+}$ at the Ga-site making it a potential candidate for use as an effective acceptor dopant, although we recognise the possible electronic contribution from mixed-valency. In our view, the dopant energies will not be modified significantly by crystal field terms of transition metal dopants since these effects are included implicitly in the interatomic potential model. We note that the potentials have been derived to reproduce the observed structures of the corresponding binary oxides.

Finally, a key point is that based on low energetics, the favourable incorporation of dopant ions (such as Sr$^{2+}$) will enhance oxygen diffusivity owing to the increase in the population of oxygen vacancies.

### 3.1.2 $M^{3+}$ substitution.
Addition of isovalent $M^{3+}$ dopants will not require charge-compensation, and can be represented by the defect reactions:

**La-site:**
\[
\frac{1}{2}M_2O_3 + \frac{1}{2}La_2O_3 \rightarrow M_{La}^3 + \frac{1}{2}La_2O_3 \tag{4}
\]

**Ga-site:**
\[
\frac{1}{2}M_2O_3 + \frac{1}{2}Ga_{Ga} \rightarrow M_{Ga}^3 + \frac{1}{2}Ga_2O_3 \tag{5}
\]

The calculated solution energies for a series of trivalent dopants are represented in Fig. 2. The results clearly confirm that cation size is a key factor: smaller ions of radius $< 0.8$ Å (including Al$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Fe$^{2+}$, Sc$^{3+}$) are predicted to be highly soluble at the Ga site, while larger rare-earth dopants (e.g. Gd$^{3+}$, Nd$^{3+}$) substitute preferentially at the La site. Our calculations are in accord with structural studies that show Gd$^{3+}$ and Nd$^{3+}$ incorporation into the La sublattice, and transition metal doping at the Ga site.

### 3.1.3 $M^{4+}$ and $M^{5+}$ substitution.
Only a few studies have examined the doping of LSGM with higher valent cations such as Ti$^{4+}$ or Nb$^{5+}$. For both $M^{4+}$ and $M^{5+}$ donor dopants, the type of charge-compensating defect has not been clearly established; for example, the following equations represent $M^{4+}$ incorporation involving either La- (V$^{''}_{La}$) or Ga-vacancy (V$^{''}_{Ga}$) compensation:

$M^{4+}$ at La with La vacancy compensation:
\[
\frac{1}{2}M_2O_3 + \frac{1}{3}La_2O_3 \rightarrow M_{La}^{4+} + \frac{1}{3}V^{''}_{La} + 2\frac{1}{3}La_2O_3 \tag{7}
\]

$M^{4+}$ at Ga with Ga vacancy compensation:
\[
MO_2 + \frac{1}{3}Ga_{Ga} + \frac{1}{3}V^{''}_{Ga} \rightarrow M_{Ga}^{4+} + \frac{1}{3}V^{''}_{Ga} \tag{8}
\]

$M^{5+}$ at Ga with La vacancy compensation:
\[
MO_2 + \frac{1}{3}Ga_{Ga} + \frac{1}{3}La_2O_3 \rightarrow M_{Ga}^{5+} + \frac{1}{3}V^{''}_{La} + \frac{1}{3}La_2O_3 \tag{9}
\]

$M^{5+}$ at Ga with Ga vacancy compensation:
\[
MO_2 + \frac{4}{3}Ga_{Ga} \rightarrow M_{Ga}^{5+} + \frac{1}{3}V^{''}_{Ga} + \frac{2}{3}Ga_2O_3 \tag{10}
\]

Therefore, the precise mode of site-substitution is critical and can be difficult to probe by experiment alone. In Table 2, we present calculated solution energies for the different modes of solutions for the cations Ti$^{4+}$, Sr$^{2+}$, Zr$^{4+}$, Hf$^{4+}$, Th$^{4+}$, Nb$^{5+}$ and Ta$^{5+}$; this constitutes a much wider survey than current experimental reports.

Three main points emerge. Firstly, all the $M^{4+}$ and $M^{5+}$ dopants (except Th$^{4+}$) show a preference for substitution at the Ga site with La vacancy (V$^{''}_{La}$) compensation; in general substitution at the La site is energetically unfavourable. Secondly, the largest cation considered, Th$^{4+}$, is the only
Table 2 Calculated solution energies (in eV per dopant ion) for M$^{4+}$ and M$^{5+}$ dopants in LaGaO$_3$ (at both La and Ga sites)  

<table>
<thead>
<tr>
<th>Dopant</th>
<th>La vacancy compensation</th>
<th>Ga vacancy compensation</th>
<th>La vacancy compensation</th>
<th>Ga vacancy compensation</th>
</tr>
</thead>
<tbody>
<tr>
<td>La site</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti$^{4+}$</td>
<td>6.04</td>
<td>6.96</td>
<td>0.83</td>
<td>0.09</td>
</tr>
<tr>
<td>Sn$^{4+}$</td>
<td>4.11</td>
<td>5.03</td>
<td>1.09</td>
<td>0.17</td>
</tr>
<tr>
<td>Zr$^{4+}$</td>
<td>3.77</td>
<td>4.69</td>
<td>0.42</td>
<td>1.34</td>
</tr>
<tr>
<td>Hf$^{4+}$</td>
<td>1.56</td>
<td>2.48</td>
<td>3.88</td>
<td>4.80</td>
</tr>
<tr>
<td>Nb$^{5+}$</td>
<td>5.27</td>
<td>7.11</td>
<td>0.25</td>
<td>2.09</td>
</tr>
<tr>
<td>Ta$^{5+}$</td>
<td>5.61</td>
<td>7.45</td>
<td>0.48</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Table 3 Calculated solution energies (in eV per dopant ion) for M$^{4+}$ dopants in LaGaO$_3$ and A-site deficient La$_{0.83}$GaO$_{2.75}$ (at both La and Ga sites)  

<table>
<thead>
<tr>
<th>Dopant</th>
<th>LaGaO$_3$</th>
<th>La$<em>{0.83}$GaO$</em>{2.75}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$^{3+}$</td>
<td>La-site</td>
<td>2.66</td>
</tr>
<tr>
<td>In$^{3+}$</td>
<td>Ga-site</td>
<td>0.94</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>La-site</td>
<td>0.38</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>Ga-site</td>
<td>0.37</td>
</tr>
</tbody>
</table>

It is known that deviations from A/B stoichiometry in perovskite oxides can strongly influence their dopant behaviour, sintering properties and chemical stability. For example, cation non-stoichiometry in the SOFC material (La,Sr)MnO$_3$ and the proton-conducting cerates (ACeO$_3$)$_5$ has been used to modify their properties. Luecke and Armstrong recently investigated the creep behaviour of lanthanum gallate deliberately prepared to give A-site deficient non-stoichiometry, Karton et al. find that the Ti and Nb-doped gallate materials exhibit lower oxygen ion conductivity.

3.2. M$^{4+}$ dopants in A-site deficient lanthanum gallate

It is known that deviations from A/B stoichiometry in perovskite oxides can strongly influence their dopant behaviour, sintering properties and chemical stability. For example, cation non-stoichiometry in the SOFC material (La,Sr)MnO$_3$ and the proton-conducting cerates (ACeO$_3$)$_5$ has been used to modify their properties. Luecke and Armstrong recently investigated the creep behaviour of lanthanum gallate deliberately prepared to give A-site deficient non-stoichiometry, Karton et al. find that the Ti and Nb-doped gallate materials exhibit lower oxygen ion conductivity.

3.3. Dopant–vacancy association

LaGaO$_3$ materials are typically acceptor-doped with divalent ions (Sr$^{2+}$, Mg$^{2+}$) with the creation of charge-compensating oxygen vacancies that are crucial to the observed ionic conductivity. It is well known that in fluorite-structured oxides (e.g. doped CeO$_2$ and ZrO$_2$) interactions between dopant ions and their opposite-charged compensating defects leads to the formation of distinct clusters (or associates). This adds a binding (association) energy term to the conduction activation energy. Dielectric relaxation measurements by Nowick et al. of acceptor-doped KTaO$_3$ and CaTiO$_3$ perovskites also provide evidence of dopant–vacancy pairs.

However, there has been conflicting debate as to whether there are any significant dopant–vacancy interactions in the lanthanum gallate perovskite. Conductivity measurements of LSGM find significant differences in activation energy as a function of Sr and Mg content. Huang et al. have noted the possible “trapping” of an oxygen vacancy at a divalent cation dopant on the Ga site. However, detailed experimental determination of the atomic structures of defect clusters can be difficult.

In an attempt to shed light on this problem we have extended our previous studies by performing a wide series of calculations on defect clusters in the LaGaO$_3$ system comprised of dopant substitutions and oxygen vacancies. For this task our simulation methods are well suited as they model accurately the electronic structure of any local association process. The cluster binding energies ($E_{\text{bind}}$) were calculated using the general relation:

$$E_{\text{bind}} = E_{\text{cluster}} - \left( \sum_{\text{component}} E_{\text{isolated defect}} \right)$$

where a negative value indicates that the cluster is stable with respect to the component isolated defects. Results for dopant–vacancy clusters involving monovalent, divalent and trivalent cations are discussed in the following sub-sections.

3.3.1 Clusters with M$^+$ or M$^{2+}$ dopants. For divalent dopants we have considered two configurations at nearest-neighbour sites: (i) a pair-cluster ($M(V'_5O_4)$) illustrated in Fig. 3 and (ii) a neutral trimer cluster ($M(V'_5O_4)M$) shown in Fig. 4. Three main points emerge from the calculated binding...
energies reported in Table 4 and Fig. 5. First, the magnitude of the binding energy varies greatly for the different dopants with the lowest value for Sr$^{2+}$ on the La site. Indeed, a near-zero binding energy is calculated for both Sr-vacancy pair and trimers, and is predicted to be a major factor in promoting the free oxygen vacancy population and the high ionic conductivity, which we noted in our previous work.\(^{41,45}\) This may be relevant to all LaMO$\text{}_3$ perovskites in which acceptor doping is achieved by partial replacement of La by Sr, as discussed by Kilner.\(^{58}\)

Second, dopant-vacancy clusters involving Mg$^{2+}$ or divalent transition metal ions at the Ga site are found to have significant binding energies, which points to greater trapping of oxygen vacancies. The lowest value relative to Mg$^{2+}$ is for the Cu$^{2+}$ dopant, which may be beneficial to conductivity. It has been suggested that Mg doping has an important role in promoting the incorporation of a higher concentration of Sr into lanthanum gallate. In the case of the cobalt dopant, we should note that it is not certain that the dopant is introduced purely in the divalent state since Co$^{3+}$ doping would not lead to charge-compensation.

Third, the trimer clusters (M$_{Ga}$V$^s_0$M$_{La}$) for all the divalent dopants on the Ga site are slightly more stable than the pair clusters (Table 4); the symmetric linear configuration with an oxygen vacancy midway between two dopant ions (Fig. 4) probably maximises the favourable interactions.

Our results for Mg are consistent with the observed increase in the conduction activation energy at higher Mg doping levels in LSGM.\(^\text{1,4}\) This would lead to two regions in the conductivity Arrhenius plot (ln $\sigma$ versus 1/$T$) as found from conductivity measurements.\(^\text{7,10,34}\) The high temperature region relates to purely the oxygen migration energy, whereas the low temperature region relates to both migration and binding energy terms, i.e. Mg-vacancy association contributes to the observed increase in activation energy at low temperatures. More recently, Norby and Haavik\(^\text{12}\) have employed simple defect models to rationalise the temperature-dependent conductivity of LSGM and derive a defect association enthalpy of $-65 \pm 5$ kJ mol$^{-1}$ which is compatible with our calculated binding energies.

Finally in this section, we also considered neutral pair clusters (M$_{La}$V$^s_0$) for both Na$^+$ and K$^+$ dopants at the La site, although we recognise that the solubility of monovalent ions is believed to be low. The resulting binding energies of up to $-0.8$ eV (Table 4 and Fig. 5) suggest strong association between these monovalent ions and oxygen vacancies, which would have a detrimental effect on ionic conductivity. Indeed, the studies of Thangadurai and Weppner\(^\text{51}\) have indicated that replacement of Sr$^{2+}$ by K$^+$ in LSGM decreases the electrical conductivity and increases the activation energy to about 1.4 eV.

### 3.3.2 Clusters with M$^{3+}$ dopants.

Previous experimental and simulation work on dopants in fluorite-oxides have indicated...
that the local “elastic strain” interaction between defects in the cluster is an important term in addition to the electrostatic interaction. Of interest here is the examination of interactions between trivalent (M\(^{3+}\)) dopants and oxygen vacancies since these isovalent substitutionals have no “effective” charges (i.e. charges relative to the host La\(^{3+}\) or Ga\(^{3+}\) lattice). We note that the oxygen vacancies have already been introduced into the lattice by acceptor dopants (e.g. Sr\(^{2+}\)).

The calculated binding energies for pair clusters (M\(^{x}\)V\(^{w}\)) are presented in Fig. 6. The results indicate a degree of association for all the trivalent dopants at either La or Ga sites, with binding energies ranging from about –0.1 to –0.45 eV. These results suggest the importance of elastic strain effects. The binding energy is dependent upon the ion size “mis-match” between host and isovalent dopant causing local perturbation with the expectation of a minimum when the ionic radii are approximately the same. This is borne out here with the greater binding energy being dependent upon the ion size mismatch for In\(^{3+}\) approximately the same. This is borne out here with the greater binding energy dependence upon the ion size mismatch for In\(^{3+}\).

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Recent work on substitution of Co for Mg in LSGM has shown a small enhancement of ionic conductivity at low levels. In addition, Ishihara et al. have observed that for rare-earth doped LaGaO\(_3\) the ionic conductivity decreases in the order Nd\(^{3+}\) > Gd\(^{3+}\) > Y\(^{3+}\). These findings are compatible with our results in which the calculated binding energy increases in the same order.

### 3.3.3 Complex Mg\(^{2+}\)-vacancy clusters.

Our results for Mg in particular suggest the importance of defect-dopant association in accord with conductivity studies. As in fluorite-oxides, the simple pair clusters are expected to dominate in the low concentration regime. At higher dopant levels more complex defect clusters are thought to come into play and may be related to possible short-range ordering. However, such local structures have not been fully investigated.

We have therefore examined, for the first time, the energetics of larger clusters focusing on Mg on the Ga site with oxygen vacancies at nearest-neighbour sites. Neutral configurations related to possible short-range ordering. However, such local structures have not been fully investigated.

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**Fig. 6** Calculated binding energies for dopant–oxygen vacancy clusters as a function of dopant ionic radius for M\(^{3+}\) ions. (Values for Sr\(^{2+}\) and Mg\(^{2+}\) are included as reference points).

**Fig. 7** 2D (in-plane) arrays of large neutral Mg\(^{2+}\)-vacancy clusters (a) (4M\(_{Ga}\)V\(^{\omega}\)); (b) (12M\(_{Ga}\)V\(^{\omega}\)). (Filled circles represent Mg and open squares vacancies; occupied oxygen sites are omitted for clarity).

**Fig. 8** 3D structures of large neutral Mg\(^{2+}\)-vacancy clusters (a) (8M\(_{Ga}\)V\(^{\omega}\)); (b) (12M\(_{Ga}\)V\(^{\omega}\)). (Filled circles represent Mg and open squares vacancies; occupied oxygen and La sites are omitted for clarity).

**Fig. 9** Calculated binding energies for 2D and 3D configurations of neutral Mg–vacancy clusters (5M\(_{Ga}\)V\(^{\omega}\)) as a function of the number of Mg\(^{2+}\) ions.
Table 5 Calculated oxidation energy (vacancy to hole) in La_{0.8}Sr_{0.2-}\textit{x}Ga_{0.8}Mg_{0.1}M_{0.1}O_{3-}\textit{x}.

<table>
<thead>
<tr>
<th>Cation, M</th>
<th>( E_{\text{ox}}/\text{eV hole}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg\textit{\textsuperscript{2+}}</td>
<td>2.18</td>
</tr>
<tr>
<td>Ni\textit{\textsuperscript{3+}}</td>
<td>-3.29</td>
</tr>
<tr>
<td>Cu\textit{\textsuperscript{2+}}</td>
<td>-2.28</td>
</tr>
<tr>
<td>Cr\textit{\textsuperscript{3+}}</td>
<td>0.90</td>
</tr>
<tr>
<td>Mn\textit{\textsuperscript{4+}}</td>
<td>2.17</td>
</tr>
<tr>
<td>Fe\textit{\textsuperscript{3+}}</td>
<td>2.18</td>
</tr>
<tr>
<td>Co\textit{\textsuperscript{3+}}</td>
<td>1.70</td>
</tr>
</tbody>
</table>

Two main points emerge. First, all the clusters show relatively favourable binding energies with the magnitude varying for the different structures. The strongest binding energy is found for the \( 4\text{Mg}\text{Ga}_{2}\text{V}_{25}^{0} \) configuration (Fig. 7). Second, the 3D structures show greater stability than the 2D arrays for the largest nano-scale \( 12\text{Mg}\text{Ga}_{6}\text{V}_{25}^{0} \) cluster. These results suggest that such complex clusters may form at higher dopant concentrations and may be important as precursors to possible short-range ordering or “nano-domain” formation. We note that recent electron diffraction studies of Politova and Irvine\textsuperscript{60} have suggested nano-domains of dopant ions and oxygen vacancies in the zirconia-based oxygen ion conductor.

3.4. Hole formation in the transition-metal doped oxide

Doping with transition-metal cations in order to introduce electronic conductivity has been of interest for developing applications of mixed conductors. We have therefore examined the energetics of hole formation in Sr/Mg and transition-metal doped LaGaO\textit{3} via the following oxidation reaction:

\[
\text{V}_{0}^{0} + \frac{1}{2}\text{O}_{2(g)} = \text{O}_{0}^{0} + 2h^{\ast}
\]  

(12)

which involves the “filling” of oxygen vacancies to create holes (h\textsuperscript{*}). Our approach to electronic defects follows that used for other LaMO\textit{3} perovskites in which we model the localised hole centre on oxygen (as O\textsuperscript{*}) or on the transition metal ion (as M\textsuperscript{3+} or M\textsuperscript{4+}).\textsuperscript{44}

We focused our calculations on the oxidation process within the \( \text{La}_{0.8}\text{Sr}_{0.2-}\text{Ga}_{0.8}\text{Mg}_{0.1}\text{M}_{0.1}\text{O}_{3-}\text{a} \) system where M is the dopant ion. Using the hole terms, the energies of the oxidation reaction (12) were calculated for all three systems and are reported in Table 5. Our analysis has included all the key terms in the solution and redox processes. There are, however, uncertainties in the absolute values due to the free-ion energies employed. Nevertheless, our concern here is to understand trends in the formation of hole species; for this task our modelling methods have proved to be reliable.

First, the calculated oxidation energy for Sr and Mg doped LaGaO\textit{3} (with oxygen hole formation) suggests an unfavourable process. This result indicates that ionic rather than electronic compensation (and hence ionic rather than p-type conductivity) predominates in LSGM which is in agreement with tracer experiments.\textsuperscript{5} Such redox behaviour is in contrast to that found in LaMO\textit{3} perovskites containing transition-metal ions at the B-site, in which a key factor for conduction behaviour is the relative ‘redox stability’ of the transition-metal cation. In general, our calculations are consistent with experimental findings that show that Sr/Mg-doped LaGaO\textit{3} system is mainly an ionic conductor with an ionic transport number close to unity.

Second, the oxidation energy for Ni and Cu doped LaGaO\textit{3} suggests a thermodynamically favourable reaction (Table 5). Thus, we would expect holes (Ni\textsuperscript{3+} or Cu\textsuperscript{3+}) to form at increasing oxygen partial pressures and that oxidation will enhance the solubility of these two dopants in the LaGaO\textit{3} host. Based on the oxidation reaction (eqn. 12) the p\textsubscript{O\textsc{2}} dependence is expected to be +\textsuperscript{1/2}. These results are consistent with conductivity studies of Long et al.\textsuperscript{46} that show increasing p-type electronic conductivity at high p\textsubscript{O\textsc{2}} with increasing Ni content. Ishihara\textsuperscript{47} also finds that the Ni-doped gallate produced the highest oxygen permeation rate. The magnitude of the calculated oxidation energy for Co\textsuperscript{3+} doped LSGM is greater than for Ni\textsuperscript{3+} or Cu\textsuperscript{2+} doped materials, suggesting that it is comparatively resistant to oxidation.

Finally, we calculate relatively unfavourable energetics for Fe\textsuperscript{3+} or Mn\textsuperscript{3+} doped LaGaO\textit{3}. While no measured values are available for direct comparison, these results are consistent with experiments\textsuperscript{3} that find that the transport number of the oxygen ion is almost unity in undoped or Fe-doped LaGaO\textit{3}, whereas that of the Ni-doped material is lower than one due to hole conduction.

4. Conclusions

Advanced simulation techniques have been used to investigate dopant site-selectivity, dopant–vacancy association and hole formation in LaGaO\textit{3}-based perovskites. Our detailed studies have produced atomic-scale information that is of relevance to the electrochemical behaviour of the gallate and of other LaMO\textit{3} perovskites. The main points are as follows:

1. Favourable energetics for dopant substitution are found for Sr\textsuperscript{2+} at La and Mg\textsuperscript{2+} at Ga in accord with general observation including recent calorimetry measurements.\textsuperscript{52} Size is important for trivalent dopant incorporation: cations of radius \( \leq 0.8 \) Å (e.g. Fe, Mn, Sc, In) are favourable on the Ga site, while larger rare-earth ions (e.g. Gd, Nd) substitute preferentially on the La site.

2. The Yb\textsuperscript{3+} dopant is found to sit at the “crossover” point in our calculated energies for La versus Ga substitution. This suggests possible “amphoteric” behaviour in which the dopant can occupy either site. Our first examination of A-site deficiency in the gallate material predicts a strong influence on the site-selectivity of Yb. Hence, dopant site-selectivity would be sensitive to the La/Ga ratio and hence to the experimental processing conditions.

3. The M\textsuperscript{3+} (Ti, Sn, Zr, Hf) and M\textsuperscript{4+} (Nb, Ta) dopants are predicted to substitute for Ga with La vacancy compensation. Such “donor” doping may facilitate La vacancy diffusion. The favourable binding energy for the \( (\text{V}_{\text{La}}^{\text{\textit{\textsuperscript{\ast}}}})^{\text{\textit{x}}} \) cluster of vacancies could be a factor inhibiting oxygen ion conductivity in samples that are M\textsuperscript{4+}/M\textsuperscript{3+} doped or A-site deficient.

4. Our results on dopant–vacancy association may have general relevance to other ABO\textit{3} perovskite oxides. The cluster binding energy (and hence activation energy) is dependent upon ion size effects and A/B site-occupancy. This is analogous to ion size effects in doped fluorite-oxides. A minimum in binding energy in LaGaO\textit{3} occurs when the ionic size of the host and dopant are close to each other (e.g. Sr\textsuperscript{2+} on La\textsuperscript{3+} and Co\textsuperscript{2+} on Ga\textsuperscript{3+}), which would be beneficial to oxygen ion conductivity. In particular, incorporation of Sr\textsuperscript{2+} at La will optimise oxygen diffusivity owing to the negligible binding energy term and the free oxygen vacancy concentration. This may be relevant to all LaMO\textit{3} perovskites in which acceptor doping is achieved by partial replacement of La by Sr.

5. Our prediction of strong Mg-vacancy association is consistent with the observed increase in the conduction activation energy at higher Mg doping levels and at low temperatures. This would lead to two regions in the conductivity Arrhenius plot.

6. Dopant–vacancy association for isovalent (M\textsuperscript{3+}) substitution indicates the importance of elastic strain effects, which depend upon the degree of ion size “mismatch” between host and dopant ion. The strongest binding energies are found for In\textsuperscript{3+} on Ga\textsuperscript{3+} and Y\textsuperscript{3+} on La\textsuperscript{3+}, which would be detrimental to oxygen ion conductivity.

7. We considered, for the first time, larger complex clusters (\( c\text{Mg}_{\text{Ga}_{0.8}V_{0.25}}^{\text{\textit{x}}} \)) of \( x \) up to 12 within 2D and 3D structures. These clusters may be important as precursors to possible short-range
ordering or “nano-domain” formation at higher dopant regimes. Indeed, one of the aims of this work is to encourage further structural studies (e.g. electron microscopy, electron diffraction) to probe such defect features in perovskite oxides at the local level.

(8) Favourable oxidation to form hole species is found for Ni$^{2+}$ and Cu$^{2+}$ doping, but not for Fe$^{2+}$ and Mn$^{2+}$ doping. This suggests p-type conductivity at increasing oxygen partial pressure with a PO$_2$ dependence of $+1/4$. Our results confirm that Ni and Cu doped LSGM are possible candidates for applications of mixed ionic-electronic conductors (e.g. SOFC cathodes, oxygen separation membranes).

5. Acknowledgements

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6. References