Defects, Dopants, and Protons in LaNbO₄

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Simulation methods have been used to investigate the energetics of defect formation, dopant solution, water incorporation, and defect clustering in the high-temperature proton conductor LaNbO₄. The interatomic potential model successfully reproduces the observed tetragonal scheelite-type structure of LaNbO₄. Formation of an oxygen vacancy, required for protonation, is accompanied by significant local relaxation leading to an [NbO₄]⁴⁻ group. The most favorable dopant solution energies are found for Ca²⁺ and Sr²⁺ on the La site. Dopant-vacancy association is predicted to occur for a wide range of divalent dopants on the La site and tetravalent dopants on the Nb site. Dopant-proton association is also predicted to occur for the range of dopants studied. The lowest M − OH⁺ binding energy is found for Ca, which is commonly used in compositions displaying the highest proton conductivities so far reported in the LaNbO₄ system.

1. Introduction

Proton transport as the principal electrical conduction mechanism in oxides at elevated temperatures is a relatively rare phenomenon which may be exploited in electrochemical devices for the production, separation or oxidation of hydrogen.1–4 Solid oxide fuel cells with proton-conducting electrolytes (protonic ceramic fuel cells, PCFCs) operate within an intermediate temperature range (400–800 °C), converting hydrogen without the need for either noble-metal catalysts or fuel recirculation at the anode.5 High levels of proton transport in oxides may also be exploited as hydrogen and humidity sensors,6–9 and in chemical reactors for various important industrial reactions, such as ammonia generation,10 and the partial oxidation11 and Reforming12 of methane. Mixed protonic-electronic conduc-

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In addition to proton transport, LaNbO$_4$ displays a number of other enticing properties. The phase transition to the monoclinic polymorph is associated with stress-induced ferroelasticity, of interest for novel energy-absorbing applications. The ferroelasticity of the monoclinic polymorph has been correlated to excellent dielectric microwave properties, as recently reported. The multifunctionality of LaNbO$_4$ extends to photoluminescence, as it emits light with blue and ultraviolet wavelengths on excitation by ultraviolet and X-ray radiation, respectively.

However, rather little is known of the defect properties of LaNbO$_4$ on the microscopic level. Computer simulation techniques are highly informative in probing the defect properties of materials on the atomic scale, as previous successful studies of ceramic oxide-ion and proton conductors have demonstrated. In this work, we employ atomistic simulation, first to reproduce the high-temperature structure of LaNbO$_4$, and then to study the defect and dopant behavior. Using these techniques, we investigate the energetic and mechanistic features of intrinsic defects, dopant and proton incorporation, and defect association.

2. Simulation Methodology

Comprehensive reviews of the atomistic simulation techniques incorporated in the General Utility Lattice Program (GULP) are available elsewhere. In brief, the simulation involves calculation of the potential energy of the system in terms of atomic coordinates, with ionic interactions described as ionic pairwise potentials. The Born model was used, in which the potential energy is partitioned into long-range Coulombic terms and short-range terms approximating Pauli repulsion and dispersive energies.

The short-range pair potentials (up to 15 Å) were specified in the Buckingham form,

$$\phi_i = A_i \exp\left(-\frac{r}{\rho_i}\right) - \frac{C_{ii}}{r^6}$$

where parameters $A_i$, $\rho_i$, and $C_{ii}$ are specific to each ion–ion interaction. Electronic polarizabilities of the ions were taken into account using the shell model developed by Dick and Overhauser.

Charged defects such as oxygen vacancies or aliovalent dopants cause significant perturbation of the surrounding lattice. The energy of such a defect relative to the perfect, energy-minimized lattice was calculated using a two-region (Mott–Littleton) approach, with the lattice partitioned into inner and outer spherical regions centered on an individual defect or defect cluster. Ions in the inner region (>1500 atoms) were relaxed explicitly, whereas the remainder of the crystal, where the defect forces are relatively weak, were treated by more approximate quasi-continuum methods.

3. Results and Discussion


The tetragonal, high-temperature structure of LaNbO$_4$, shown in Figure 1, is isostructural with scheelite (CaWO$_4$), with the Nb$^{5+}$ cations residing in undistorted NbO$_4$ tetrahedra. To model the crystal structure, initial sets of potential parameters were taken from the literature and fitted to the reported scheelite-type structure of LaNbO$_4$ under constant pressure conditions. Phonon densities of states were also calculated to confirm the structure was stable. The final potential parameters and calculated structural parameters are listed in Tables 1 and 2, respectively. The agreement with unit-cell parameters and bond lengths obtained from neutron diffraction is very good (Table 2). The calculated dielectric constants, although not reproducing the experimental values reported for LaNbO$_4$ exactly, are on the same order of magnitude. Given the uncertainties typically associated with dielectric-constant measurements, and the approximations...
of the model, the calculated value is satisfactory. The difference is unlikely to have a drastic effect on the calculated properties or energies, particularly the relative energies and overall trends. The calculated elastic constants are also listed in Table 2, although to the best of our knowledge, no experimentally determined elastic properties for high-temperature LaNbO₄ have yet been reported.

Intrinsic defects in an ionic solid, including Frenkel- and Schottky-type disorder, can give rise to intrinsic diffusion of ions. However, such point defects are difficult to study experimentally on the atomic scale. Simulation techniques enable these defects to be examined with atomic resolution, and thus provide a useful probe of intrinsic defect behavior. In this study, the energies of isolated intrinsic defects such as vacancies and interstitials were calculated, from which the enthalpies of the various Frenkel and Schottky disorder types were determined. The calculation of the latter also required calculation of the lattice energies of La₂O₃, Nb₂O₅, and LaNbO₄. The resulting defect energies are listed in Table 3.

The most favorable intrinsic disorder type in LaNbO₄ is the O Frenkel defect (Table 3), although its magnitude indicates that a negligible concentration of such species will be present. The La Frenkel defect requires substantially more energy, whereas the energy of the Nb Frenkel defect could not be determined because of the inability of the structure to accommodate Nb⁵⁺ interstitial ions with their high charge.

The arrangement of Nb—O₄ tetrahedra around an oxygen vacancy is shown schematically in Figure 2. Significant relaxation of Nb—O₄ tetrahedra about the oxygen vacancy results in the formation of an [Nb₂O₇]⁴⁻ group (Figure 2b), with two tetrahedra corner-sharing an oxygen. This is facilitated by rotation of the nearer of the two [NbO₄]³⁻ tetrahedra in the [Nb₂O₇]⁴⁻ group to the vacancy defect center with respect to the perfect structure. We note that condensation of two or three Nb—O₄ units around a doubly ionized oxygen vacancy forming an [NbO₃]⁴⁻ or [NbO₁₁]⁻ group has been reported recently by Kuwabara et al. based on DFT calculations.

Given the similarity of the double-tetrahedral units we find here to those which form in the La₁₋ₓGaₓO₄₋ₓ/2 ionic conductor, we conjecture that oxide-ion transport in LaNbO₄ also involves the breaking and reforming of the [Nb₂O₇]⁴⁻ units in a cooperative “cogwheel-type” process, as in the gallate. Further examination of this process, for example, by molecular dynamics, while beyond the scope of the present study, needs to be undertaken.

### Table 3. Frenkel and Schottky Disorder

<table>
<thead>
<tr>
<th>type</th>
<th>defect equation</th>
<th>energy (eV/defect)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La Frenkel</td>
<td>La⁺⁺O⁻⁺ → La⁺⁺O⁻⁻ + V′⁺⁺</td>
<td>7.45</td>
</tr>
<tr>
<td>O Frenkel</td>
<td>O⁻⁻ → O⁻⁻ + F⁻⁻</td>
<td>3.55</td>
</tr>
<tr>
<td>Schottky</td>
<td>La⁺⁺O⁻⁻ + Nb⁺⁺ + 4O⁻⁻ → V′⁺⁺ + V″⁻⁻ + 4F⁻⁻ + La⁺⁺ + Nb⁺⁺</td>
<td>5.60</td>
</tr>
<tr>
<td>La Schottky-type</td>
<td>2La⁺⁺O⁻⁻ + 3O⁻⁻ → 2V′′⁺⁺ + 3F⁻⁻ + La⁺⁺O⁻⁻</td>
<td>4.08</td>
</tr>
<tr>
<td>Nb Schottky-type</td>
<td>2Nb⁺⁺ + 5O⁻⁻ → 2F′⁻⁻ + 5F⁻⁻ + Nb⁺⁺O⁻⁻</td>
<td>6.62</td>
</tr>
</tbody>
</table>


where $M$ represents the aliovalent dopant. The interatomic potentials for the dopant cations were taken from studies of the corresponding binary metal oxides.\(^{(42-46)}\) The energies of the above reactions were then evaluated by combining the corresponding defect- and lattice-energy terms. The calculated solution energies as a function of ionic radius for LaNbO$_4$ are plotted in panels a and b in Figure 3 for substitution on the La and Nb sites, respectively.

Two main points emerge from these results. First, the most favorable dopants for substitution on the La site are Ca$^{2+}$ and Sr$^{2+}$. These dopants are associated with the highest proton conductivity reported to date for LaNbO$_4$.\(^{(19,20)}\) That these dopants exhibit the lowest solution energies may be rationalized in terms of their similar size\(^{(47)}\) to the host cation: 1.12 Å for Ca$^{2+}$ and 1.26 Å for Sr$^{2+}$ in 8-fold coordination compared with 1.16 Å for La$^{3+}$. The high solution energies of other divalent dopants with ionic radii much larger or smaller than La implies that lattice strain due to ion-size mismatch plays a significant role in determining dopant solubility. A similar phenomenon has been observed in fluorite- and perovskite-based ion conductors. Second, the solution energy associated with doping on the Nb site also shows a strong dependence on ionic radii, with the dopants Ti$^{4+}$ ($r_{Ti^{4+}} = 0.42$ Å),\(^{(47)}\) Sn$^{4+}$ (0.55 Å), and Zr$^{4+}$ (0.59 Å), of similar ionic radii to the host Nb$^{5+}$ cation (0.48 Å), showing the lowest solution energies.

Extrinsic oxygen vacancies formed on doping with subvalent cations can be trapped by the dopant, as is well documented,\(^{(48)}\) leading to defect clustering and to higher activation energies for oxide-ion conductivity. The effects of defect clustering are important in oxide-ion-conducting perovskite systems, but have not been studied in the LaNbO$_4$ system. Whereas trapping of oxide-ion vacancies is evidently disadvantageous for applications involving oxide-ion transport, similar phenomena in proton-conducting oxides may have both beneficial and detrimental effects. For proton-conducting electrolytes, high levels of oxide-ion conductivity are undesirable. However, mixed proton and oxide-ion conductivity in ceramic membranes, giving rise to steam permeation, provides a method of direct hydrocarbon reforming in the anode compartment of a PCFC, in addition to having other potential applications.\(^{(49,50)}\)

The energies of defect clusters in LaNbO$_4$ were evaluated based on simple pair clusters ($M^-V_{O}^+$) of a divalent or tetravalent dopant ion and nearest neighbor oxygen vacancy. The pair-cluster binding energies, shown in Table 4 for the most favorable divalent and tetravalent dopant species, respectively, were calculated according to

$$E_{bind} = E_{cluster} - \Sigma E_{isolated\ defects}$$  \hspace{1cm} (4)


Inspection of Table 4 reveals that the pair-defect cluster energies are favorable for all divalent and tetravalent dopants examined. It is expected, therefore, that clustering, with its associated higher oxide-ion migration energies and thus lower oxide-ion diffusion coefficients, may be significant in doped LaNbO$_4$. We note that for the range of divalent and tetravalent dopants examined here, lower binding energies are observed with increasing dopant ion radius.

### 3.3. Water Incorporation and Dopant-Proton Association

Incorporation of mobile protons in the LaNbO$_4$ structure is understood to involve filling of oxygen vacancies with hydroxyl groups in wet or hydrogen-containing atmospheres, with the second proton attaching itself to a lattice oxygen

$$\text{H}_2\text{O} + \text{O}^\cdot + V_0^\cdot \rightarrow 2\text{OH}^\cdot$$ (5)

The energetics of water incorporation were evaluated using the same methodology as that employed in previous studies of proton-conducting oxides\(^{(51)}\) according to

$$E_{\text{H}_2\text{O}} = 2E_{\text{OH}} - E_{V_0^\cdot} + E_{\text{PT}}$$ (6)

where $E_{\text{OH}}$ is the energy associated with replacing an O$^2-$ ion with an OH$^-$ group, $E_{V_0^\cdot}$ is the energy needed to create an oxygen vacancy, and $E_{\text{PT}}$ is the energy of the gas-phase reaction O$^2-$ + H$_2$O = 2OH$^-$.\(^{(52)}\) A Morse potential was used to model the attractive O–H interaction

$$V(r) = D\{1 - \exp[-\beta(r - r_0)]\}^2$$ (7)

using parameters (Table 5) developed from ab initio quantum mechanical cluster calculations,\(^{(53)}\) with a point charge representation of the surrounding lattice. The dipole moment of the O–H group was included by placing charges of 1.4263 and \(0.982\) on the O and H species, respectively (to give an overall charge of \(1^-\)), and the interaction between lattice oxygens and the hydroxyl group was taken into account with an additional Buckingham potential term.\(^{(54)}\) Table 6 lists the calculated values for $E_{\text{OH}}$, $E_{\text{H}_2\text{O}}$, and the O–H bond length after relaxation.

As with previous studies,\(^{(55,56)}\) our simulation technique may be used to probe the proton site and investigate the most energetically favorable O–H configuration. After structural relaxation, the proton is oriented toward a neighboring oxygen along an edge of the Nb–O$_4$ tetrahedron, as shown schematically in Figure 4. The equilibrium O–H distance, 0.98 Å, has not been reported previously for LaNbO$_4$. This value is very similar to that determined by atomistic simulation for the proton-conducting perovskite oxides SrCeO$_3$ (0.986 Å)\(^{(57)}\) and BaCeO$_3$ (0.99 Å).\(^{(58)}\)

<table>
<thead>
<tr>
<th>Morse potential</th>
<th>$D$ (eV)</th>
<th>$\beta$ (Å$^{-1}$)</th>
<th>$r_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O···H</td>
<td>7.0525</td>
<td>2.1986</td>
<td>0.9485</td>
</tr>
<tr>
<td>Buckingham potential</td>
<td>$A$ (eV)</td>
<td>$\rho$ (Å)</td>
<td>$C$ (eV Å$^6$)</td>
</tr>
<tr>
<td>O···H</td>
<td>311.97</td>
<td>0.2500</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 5. Parameters for the O–H Interaction

$E_{\text{OH}}$ (eV)$^a$ | $E_{\text{H}_2\text{O}}$(eV) | O–H (Å) |
<table>
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<tr>
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<tbody>
<tr>
<td>15.16</td>
<td>−0.25</td>
<td>0.982</td>
</tr>
</tbody>
</table>

$^a$ Includes Morse potential.

Figure 4. Orientation of proton (blue) relative to an [NbO$_4$]$^{3-}$ tetrahedron.

Haugsrud and Norby report a hydration enthalpy of approximately $-1.2$ eV for La$_{0.99}$Ca$_{0.01}$NbO$_4$$\cdot$$O_4$ determined from conductivity studies,\(^{(19,20)}\) which is slightly less negative than better proton conductors such as acceptor-doped SrCeO$_3$ and BaCeO$_3$. Our model also gives a negative value of $-0.25$ eV for the hydration energy, consistent with the exothermic uptake of protons from water in the atmosphere. A possible explanation for the calculated value not being as negative as the measured value is that the former does not include the influence of grain boundaries on the energetics of water absorption. It is worth noting that grain boundaries play an important role in proton absorption and transport in wet atmospheres in the low-temperature range.\(^{(27,59)}\) Fjeld et al.\(^{(58)}\) have noted that protons are the major charge carriers in the grain boundaries at 400 °C where the monoclinic LaNbO$_4$ polymorph stabilizes, although the grain-boundary conductivity is much lower than that of the grain interior. Similar behavior is likely for the tetragonal form as well. Future simulation studies of protons at grain boundaries in this material could help shed light on this intriguing phenomenon.

Because of their net positive charge relative to the lattice, protons may associate with subvalent dopant species, in an analogous manner to dopant-vacancy association, with a concomitant decrease in proton mobility. Proton-trapping effects have been observed experimentally\(^{(59,60)}\)

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and simulated by both quantum mechanical and atomistic techniques in other proton-conducting oxides. Recent neutron-spin–echo experiments on proton dynamics in hydrated \( \text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95} \) indicate that the proton spends an extended time in the vicinity of a dopant Y cation prior to further diffusion.

The binding energy associated with a cluster comprised of an OH group and an adjacent dopant cation was calculated as the difference between the sum of the isolated defects and the cluster energy

\[
E_{\text{bind}} = E(M^i - \text{OH}_0) - \{E(M^i) + E(\text{OH}_0)\} \tag{8}
\]

The negative values for the binding energies, shown in Table 4, indicate that \( M_{\text{Nb}} - \text{OH}^* \) and \( M_{\text{La}} - \text{OH}^* \) clusters are likely to form, with the lowest binding energies found for many different dopants, \( \text{Ca}^{2+} \) and \( \text{Sr}^{2+} \) are the species which are reported to produce the most appreciable proton transport. These results indicate that proton mobility is very sensitive to the type of acceptor dopant ion, and may be related to basicity as well as ion-size factors.

An analogy may be drawn with the \( \text{SrCeO}_3 \) proton-conducting system, in which the \( \text{Y}^{3+} \) and \( \text{Yb}^{3+} \) dopants most often associated with high proton conductivity were found to have the lowest \( M^i - \text{OH}^* \) binding energies. The results of both studies suggest the important influence of ion-size mismatch and elastic strain between host and dopant on proton-trapping in solid-state proton conductors. The minimum binding energy should thus occur when the ionic radii of dopant and host are approximately the same.

4. Conclusions

Computer modeling techniques have been used to examine the energetics of defects, dopants and clustering in scheelite-type \( \text{LaNbO}_4 \). This study is relevant to the potential applications of \( \text{LaNbO}_4 \), in particular electrochemical devices based on the proton-conducting properties of the doped system. The main results can be summarized as follows.

(1) The simulation model successfully reproduces the observed complex scheelite-type \( \text{LaNbO}_4 \) structure. The energies calculated for intrinsic atomic defects are relatively high. The formation of an oxygen vacancy is accompanied by rearrangement of the adjacent \( [\text{NbO}_4]^{3-} \) tetrahedra to form an \( [\text{Nb}_2\text{O}_7]^{4-} \) unit.

(2) Dopant substitution is found to be most favorable for \( \text{Ca}^{2+} \) and \( \text{Sr}^{2+} \) on the La site; the similar size of these dopants to the host cation indicates the importance of minimizing elastic strain on acceptor doping. Solution on the Nb site is of higher energy but, as for doping on the La site, the most favorable dopants are those of similar ionic radii to Nb, namely \( \text{Ti}^{4+}, \text{Sn}^{4+} \), and \( \text{Zr}^{4+} \). Dopant-vacancy association is predicted to be favorable for simple pair clusters \( M_{\text{La}} - \text{V}_\text{O} \).

(3) Water dissolution is calculated to be exothermic with an equilibrium O–H distance of 0.98 Å. Binding energies for \( M^i - \text{OH}^* \) pairs are calculated to be favorable for all examined dopants. The weakest association is found for \( \text{Ca}^{2+} \), one of the dopants associated with the highest proton conductivity in \( \text{LaNbO}_4 \). This indicates that elastic strain not only influences dopant incorporation energies but also the proton-trapping energy, which is minimized for dopants with similar ionic radii to the host cation.

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