Defect formation in In$_2$O$_3$ and SnO$_2$: a new atomistic approach based on accurate lattice energies

Qing Hou,$^{a,}$* John Buckeridge,$^{a}$ Tomas Lazauskas,$^{a}$ David Mora-Fonz,$^{a}$ Alexey A. Sokol,$^{a}$ Scott M. Woodley$^{b}$ and C. Richard A. Catlow$^{a,*}$

We present a consistent interatomic force field for indium sesquioxide (In$_2$O$_3$) and tin dioxide (SnO$_2$) that has been derived to reproduce lattice energies and, consequently, the oxygen vacancy formation energies in the respective binary compounds. The new model predicts the dominance of Frenkel-type disorder in SnO$_2$ and In$_2$O$_3$, in good agreement with $ab$ initio defect calculations. The model is extended to include free electron and hole polarons, which compete with charged point defects to maintain charge neutrality in a defective crystal. The stability of electrons and instability of holes with respect to point defect formation rationalises the efficacy of n-type doping in tin doped indium oxide (ITO), a widely employed transparent conducting oxide in optoelectronic applications. We investigate the clustering of Sn substitutional and oxygen interstitial sites in ITO, finding that the dopants substitute preferentially on the cation crystallographic d site in the bixbyite unit cell, in agreement with experiment. The force field described here provides a useful avenue for the investigation of the defect properties of extended transparent conducting oxide systems, including solid solutions.

1. Introduction

The combination of high optical transparency and high electrical conductivity in transparent conducting oxides (TCOs) results in the class of materials being widely used in many fields, including solar cells, liquid crystal displays, electrochromic plating and smart windows.$^{1-3}$ The most commonly used n-type TCO materials are SnO$_2$ and In$_2$O$_3$, which tend to be oxygen deficient due to the appearance of oxygen vacancies,$^{4-7}$ and tin-doped In$_2$O$_3$ (indium tin oxide, ITO). The n-type conductivity has intuitively been attributed to the presence of these vacancies, but other sources have also been proposed$^{8-11}$ and the matter remains a topic of debate. Accurate modelling of intrinsic and extrinsic defects is needed to understand the source of conductivity. This paper reports a comprehensive survey of the defect structure of these materials and of the relationship between their defect and electronic properties. Fully $ab$ initio approaches to such problems are limited by both computational resources and methodological problems in the study of charged defects. Computational techniques based on interatomic potentials, in contrast, are particularly well suited to explore such systems, but require sufficiently accurate and transferable parameterisation. As shown below, previous work on the parameterisation of interatomic potentials suffered from a number of problems related to transferability and/or accuracy in the reproduction of essential physical properties of both parent SnO$_2$ and In$_2$O$_3$ compounds. In this paper, we demonstrate the first transferable interatomic potential model that reproduces well the physical properties of SnO$_2$ and In$_2$O$_3$ including their dielectric response and lattice energies. We then apply our methodology to develop a consistent and reliable set of models for the defect structure of the materials.

At low temperature and ambient pressure, In$_2$O$_3$ adopts the body-centred cubic bixbyite crystal structure (space group No. 206, $Ia3$, $a = 10.117$ Å), which contains 80 atoms i.e. 16 formula units in its conventional cubic unit cell. The structure can be viewed as a $2 \times 2 \times 2$ supercell of the fluorite (CaF$_2$) lattice with one fourth of the anionic sites vacant, which results in two types of cationic sites, 8b and 24d in Wyckoff’s notation, as illustrated in Fig. 1. These structural vacant sites (Wyckoff 16c) provide interstitial sites and, as discussed below, interstitial oxygen can play a key role in the properties of ITO as the
formation of such defects can compensate n-type carriers, which will detrimentally affect the conductivity.

After Rupprecht\textsuperscript{12} first carried out the study on the optical and electrical properties of In\textsubscript{2}O\textsubscript{3} in 1950s, In\textsubscript{2}O\textsubscript{3} and ITO have attracted considerable experimental and theoretical interest. Regarding the latter, there have been several studies on their electronic structure using quantum mechanical techniques.\textsuperscript{13–17} Using the local density approximation (LDA) and a LDA+U approach in Density Functional Theory (DFT), Reunchan \textit{et al.}\textsuperscript{16} proposed that the oxygen vacancy is a double donor, while the indium vacancy is a triple acceptor in indium oxide; while Ágoston \textit{et al.}\textsuperscript{17} investigated electron compensation in SnO\textsubscript{2} and In\textsubscript{2}O\textsubscript{3} using hybrid DFT and reported both SnO\textsubscript{2} and In\textsubscript{2}O\textsubscript{3} to be highly n-type dopable against the formation of intrinsic acceptors.

Methods based on interatomic potentials, while not allowing details of the electronic structure to be probed, do allow the exploration of much larger systems.\textsuperscript{18–21} Walsh \textit{et al.}\textsuperscript{22} have investigated the formation of intrinsic point defects including all possible vacancies and interstitials in indium oxide using an accurate interatomic potential. The anion Frenkel pair is reported to be the predominant form of ionic disorder due to the presence, as noted above, of intrinsic interstitial sites in the lattice. Warschkow \textit{et al.}\textsuperscript{23} explored clustering of oxygen interstitials with tin dopants in ITO using both atomistic (interatomic potential based) and DFT calculations. Strong preference was found for the formation of neutral defect clusters consisting of two substitutional Sn ions bound to an interstitial oxygen. Experimental studies have suggested that defect clusters of substitutional tin and interstitial oxygen should form in ITO.\textsuperscript{24} The Sn\textsubscript{6}\textsubscript{In} defect is positively charged (here we use the standard Kröger–Vink notation when describing defects, where * signifies a positive charge, ' a negative charge and × a neutral charge), which can compensate negatively charged O\textsubscript{6}‘. Moreover, it is argued that the formation of oxygen interstitials will lead to lattice stress, while the Sn\textsubscript{6}\textsubscript{In} ion can relieve some of this stress due to its smaller size.

For TCO materials, native defects may act as donors resulting in intrinsic n-type conductivity as has been recently demonstrated by Buckeridge \textit{et al.}\textsuperscript{25} Further extrinsic doping such as Sn in In\textsubscript{2}O\textsubscript{3} is, however, required to achieve technologically desired concentrations of charge carriers. Hence, the main aim of this work is to explore defect properties of both SnO\textsubscript{2} and In\textsubscript{2}O\textsubscript{3} and the effects of defects on the electronic properties and structure of these materials. A new set of interatomic potentials is derived and applied which accurately reproduce the elastic and structural properties of the two binary oxides. In particular, atomistic simulations are used to investigate the energetics of point defects and intrinsic disorder in In\textsubscript{2}O\textsubscript{3} and SnO\textsubscript{2}. The interatomic potential model, including a suitable approach to reproduce the fundamental band gaps, is shown to give reasonable intrinsic defect formation energies (in comparison with more accurate but computationally expensive electronic structure methods), indicating that the defect properties are modelled well. Furthermore, the formation energies of clusters of an oxygen interstitial surrounded by one or more tin substitutional defects in indium oxide are calculated and analysed. The results help explain experimental observations regarding the configurations of tin clusters in ITO.

\section{Methodology}

The lattice and defect energies in this paper are based on the Born model of the ionic solid.\textsuperscript{26} The pairwise interactions between the ions are modelled by a combination of the Buckingham,\textsuperscript{27} Lennard-Jones, constant offset and polynomial harmonic potentials to describe smooth monotonically decaying functions as shown in Fig. 2. Previously derived potential functions are also shown for comparison. In the range of bonding distances, our potentials typically have a similar gradient to the previous models, but are shifted down in energy, which, allowed us to reproduce the experimentally observed lattice energies – a key feature of our new models. Importantly, we have common oxygen parameters for SnO\textsubscript{2} and In\textsubscript{2}O\textsubscript{3}.

One significant new feature in our model is the addition of a repulsive $1/r^4$ potential, which helps to reproduce the rutile structure as the ground state for SnO\textsubscript{2}, and penalise a hypothetical anatase phase of this material. One possible rationalisation is that the unusual trigonal coordination of oxygen in a rutile environment results in its higher-order polarisability (deformation), which is not accounted for by the standard shell model. This potential could help to maintain the balance of the induced multipolar interactions in SnO\textsubscript{2}.

The Buckingham potential has the form:

\begin{equation}
U_{ij}^{\text{Buckingham}} = A_{ij} e^{\frac{-r_{ij}}{r_0}} - \frac{C_{ij}}{r_{ij}^6}.
\end{equation}

\textbf{Fig. 1} Lattice sites in In\textsubscript{2}O\textsubscript{3}. In the bottom figure, the coordination of the cations is shown, with indium ions represented by larger purple spheres and oxygen ions by smaller red spheres.
Aij

where \( r_{ij} \) is the distance between ions of species \( i \) and \( j \), \( A_{ij} \), \( \rho_{ij} \) and \( C_{ij} \) are the parameters for each interacting pair. The generalised Lennard-Jones potential has the following form:

\[
U_{\text{Lennard-Jones}} = \frac{A_{ij}}{r_{ij}^{\rho_{ij}}} - \frac{C_{ij}}{r_{ij}^{\rho_{ij}}}
\]

and \( A_{ij} \) and \( C_{ij} \) are constants, the exponents \( m \) and \( n \) are typically integers. The polynomial potential is

\[
E_{\text{Polynomial}} = C_0 + C_1(r - r_0) + C_2(r - r_0)^2 + \ldots + C_n(r - r_0)^n,
\]

and \( C_0, C_1, C_2, \ldots, C_n \) and \( r_0 \) are constants. An alternative harmonic polynomial function is given by:

\[
E_{\text{Harmonic-Polynomial}} = (r - r_0)^2(C_0 + C_1r + C_2r^2 + \ldots + C_nr^n).
\]

To model polarisable ions, we employ the shell model,\(^{28}\) where the shell (charge \( Y \)) is connected to the core by a harmonic spring (spring constant \( k \)) with the total charge equal to the charge assigned to the ion, which in the present case is the formal charge. The harmonic polarisability \( \alpha \) in \textit{vacuo} is given as:

\[
\alpha = \frac{Y^2}{k}.
\]

A careful choice of the potential parameters is crucial for the accurate modelling of both the structural and physical properties, which we will address in Section 3.1 below. The parameters of our model are given in Table 1.

The resulting potentials were used to study point defects in both In\(_2\)O\(_3\) and SnO\(_2\), using the Mott–Littleton method\(^{29,30}\) as implemented in the General Utility Lattice Package (GULP).\(^{31}\) Within the Mott–Littleton approach, the defective structure is divided into three regions with the point defect at the centre of the inner spherical region (region I). Interactions between atoms in region I are treated most accurately with explicit relaxation; beyond region I, the defect is treated in a linear-response approximation, where ionic displacements are calculated based on a harmonic representation of the true potential energy surface with an explicit account of all forces on ions in the nearest spherical shell region IIa and a more approximate treatment of the further region IIb extending to infinity, where only long-range Coulomb interactions with the defect are considered. In this work, the radius of region I is chosen as 15 Å (so that there are 1093 atoms for In\(_2\)O\(_3\) and 1189 for SnO\(_2\) in the region) with a 30 Å radius for region IIa, which corresponds to the 15 Å cut-off used in the force field parameterisation. Our tests show that this choice provides an acceptable convergence of defect energies to ca. 0.1 eV or better with relatively low computational costs. The defect energy is defined as the energy required to form a point defect in the system by adding or removing constituent ions in their formal charge states from the gas phase (or vacuum) where the energy of such gas phase ions is set to zero. Defect energies resulting from Mott–Littleton calculations can in turn be used to calculate defect formation energies that refer to atoms removed from or

| Interaction | \( \Delta \) (eV) | \( \rho \) (Å) | \( C \) (eV Å\(^6\)) |
|-------------|-----------------|-------------|-------------------|
| Sn shell–O shell | 1805.11 | 0.32 | 0.00 |
| In shell–O shell | 1937.36 | 0.32 | 30.00 |
| O shell–O shell | 24.66 | 0.50 | 32.61 |
| O core–O shell | 4194.48 | 0.20 | 0.00 |

| Interaction | \( A \) (eV Å\(^m\)) | \( B \) (eV Å\(^n\)) | \( m \) | \( n \) |
|-------------|-----------------|-------------|------|------|
| Sn core–Sn shell | 0 | 2.00 | 12 | 6 |
| Sn shell–Sn shell | 7.89 | 0 | 4 | 0 |
| Sn shell–O shell | 1 | 0 | 18 | 1 |
| In shell–In shell | 0 | 28 | 12 | 6 |
| In shell–In shell | 0 | 1 | 18 | 1 |
| In shell–O shell | 0 | 1 | 18 | 1 |
| O core–O shell | 10 | 0 | 12 | 6 |

(a) Buckingham potential
(b) Lennard-Jones potential
(c) Polynomial potential
(d) Polynomial harmonic potential
(e) Shell model

\( m \) and \( n \) are the parameters for each interacting pair. The harmonic spring constant \( k \) is connected to the core by a harmonic spring (spring constant \( k \)) with the total charge equal to the charge assigned to the ion, which in the present case is the formal charge. The ionic polarisability \( \alpha \) in \textit{vacuo} is given as:

\[
\alpha = \frac{Y^2}{k}.
\]

A careful choice of the potential parameters is crucial for the accurate modelling of both the structural and physical properties, which we will address in Section 3.1 below. The parameters of our model are given in Table 1.

Table 1: Interatomic potential parameters for SnO\(_2\) and In\(_2\)O\(_3\)

- **Interatomic potential model for In\(_2\)O\(_3\) and SnO\(_2\).** Metal–oxygen interactions are shown in the top panel, while metal–metal and oxygen–oxygen interactions are shown in the bottom panel. Our model is compared with other previously published ones (see the text for details).

- **Defect formation energies** that refer to atoms removed from or added to the crystal lattice.

- **Mott–Littleton calculations** can be used to calculate defect formation energies that refer to atoms removed from or added to the crystal lattice.

- **Gas phase ions** are set to zero. Defect energies resulting from Mott–Littleton calculations can in turn be used to calculate defect formation energies that refer to atoms removed from or added to the crystal lattice.

- **Convergence of defect energies to** ca. 0.1 eV or better with relatively low computational costs.
added to their standard states to obtain energies of solution or of redox processes and can be combined to calculate e.g. Schottky and Frenkel formation energies.

3. Results

3.1. Interatomic potentials

The first interatomic potentials for SnO$_2$ reported by Freeman and Catlow$^{32}$ were fitted to static and high frequency dielectric and elastic constants of SnO$_2$; the lattice energy and lattice parameter though were less well described, as shown in Table 2. A parameterisation of the Buckingham potential for In$_2$O$_3$, based on the oxide parameters of Freeman and Catlow$^{32}$ and Bush et al.$^{27}$ with In–O parameters of McCoy et al.$^{33}$ was reported by Warschkow et al.$^{33}$ in which the dielectric properties were not, however, fitted. Walsh et al.$^{32}$ reported an alternative parameterisation, which in contrast reproduced well the static and high-frequency dielectric constants (see Table 3), but the lattice energy again deviated from experiment and the oxide parameters were incompatible with Freeman’s SnO$_2$ potentials.

In order to describe the crystal properties of both binary oxides and ITO, it is necessary to construct a common interatomic force field for In$_2$O$_3$ and SnO$_2$ (as summarised in Table 1), which reproduces well the structure and dielectric constants. The new model was obtained by empirical fitting, using the GULP code, to calculate lattice parameters, lattice energy, and static and high-frequency dielectric constants and gave a better agreement with the experimental data compared to earlier work, as shown in Tables 2 and 3.

### Table 2: Calculated and experimental crystal properties of SnO$_2$

| Parameter                        | Experimental | Present work | Freeman and Catlow$^{32}$ |
|----------------------------------|--------------|--------------|---------------------------|
| Lattice parameter, $a$ (Å)       | 4.737$^{35}$, 4.738$^{36}$ | 4.742 | 4.706 |
| Static dielectric constant       | 14.0$^{37}$  | 16.724 | 13.8 |
| High frequency dielectric constant | 3.785$^{17}$ | 3.889 | 3.894 |
| Lattice energy (eV)              | $-122.125$  | $-122.32$ | $-110.68$ |
| Elastic constants$^{38}$         |              |              |                           |
| $C_{11}$ (GPa)                   | 261.7        | 290.55       | 299                       |
| $C_{12}$ (GPa)                   | 177.2        | 191.07       | 212                       |
| $C_{13}$ (GPa)                   | 156.0        | 249.45       | 198                       |
| $C_{33}$ (GPa)                   | 450.0        | 620.61       | 522                       |
| $C_{44}$ (GPa)                   | 103.07       | 119.20       | 111                       |
| $C_{66}$ (GPa)                   | 207          | 236.36       | 228                       |

In the following sections we use the new model to explore the defect and electronic properties of the materials.

3.2. Electron and hole formation

Although methods based on interatomic potentials are incapable of calculating the electronic structure or electron states directly, it is still possible to estimate crudely the band gap hypothesising that the valence band maximum can be represented by a hole localised on an anion, the conduction band minimum can be represented by an electron on a cation, and the difference in energy between the two gives the energy gap. Such an assumption is broadly supported by ab initio calculations on ionic compounds of most metals, including both SnO$_2$ and In$_2$O$_3$. In our model, the hole state is obtained by the instantaneous ionisation of an oxide ion including high-frequency dielectric response (via shell relaxation) to form an O$^-$ ion on an oxide ion site (the O$_0^-$ defect). As the on-site energy contributions – beyond dipolar polarisation – are not accounted for by the model, we also customarily subtract from the calculated ionisation potential the second O electron affinity (9.41 eV adopted from T. C. Waddington$^{34}$, cf. 8.75 eV from Freeman and Catlow$^{32}$, 8.89–9.58 eV from Ladd and Lee$^{39}$). For the electron, the localised state would be the Sn$^{3+}$ (for SnO$_2$) or In$^{2+}$ (for In$_2$O$_3$) ion on the appropriate cation site (Sn$_{ox}$ or In$_{ox}$ in the defect notation); the on-site fourth (third) ionisation potential of the gas phase Sn (In) is subtracted from the respective defect energy. All energy terms used to calculate the required quantities are collected in Table 4 for SnO$_2$ and Table 5 for In$_2$O$_3$.

The calculated band gap of SnO$_2$, by this crude procedure, is 5.21 eV, compared with the experimental value of 3.6 eV$^{39}$. For In$_2$O$_3$, we calculate the band gap of 6.71 eV, as compared to the experimental value of 2.7 eV$^4$ (these experimental values are fundamental band gaps, so that excitonic effects, which we do not attempt to model in our procedure, are not included). Whereas the position of the valence band is determined by these calculations quite accurately (within $\sim$ 0.5 eV of available experimental data$^{42-43}$), the conduction band is severely underbound, which can be clearly related to the one-site localisation model for an electron. While the latter approximation is reasonable for a hole, electrons in the conduction band are well known to be strongly delocalised. We will therefore use the difference between the calculated and experimental band gaps as a measure of electron localisation, which can subsequently be employed as a parameter of the electronic structure in

### Table 3: Calculated and experimental crystal properties of In$_2$O$_3$

| Parameter                        | Experimental | Present work | Walsh et al.$^{32}$ | Warschkow et al.$^{33}$ | McCoy et al.$^{33}$ |
|----------------------------------|--------------|--------------|---------------------|------------------------|---------------------|
| Lattice parameter, $a$ (Å)       | 10.117$^{44}$| 10.119       | 10.121              | 10.120                 | 10.115              |
| Static dielectric constant       | 8.9–9.5$^{45}$| 9.191        | 9.052               | 6.872                  | 9.455               |
| High frequency dielectric constant | 4$^{46}$     | 3.941        | 3.903               | 3.534                  | 4.907               |
| Lattice energy (eV)              | $-149.98$    | $-150.01$    | $-140.60$           | $-141.91$             | $-141.14$           |
| Elastic constants                |              |              |                     |                        |                     |
| $C_{11}$ (GPa)                   | 337.14       | 297.75       | 368.10              | 324.4                  | 120.7               |
| $C_{12}$ (GPa)                   | 154.99       | 141.78       | 150.11              | 151.7                  |                    |
| $C_{44}$ (GPa)                   | 93.19        | 76.42        | 111.24              | 120.7                  |                    |
In the centre of an unoccupied oxygen octahedron, there is a lower energy for an oxide ion compared to the 4g site explored by Freeman and Catlow,32 by about 0.27 eV. Of the two available cationic interstitial sites, the 4c site is more stable than 4g by 2.44 eV.

For In2O3, there are two symmetry-unique cation 6-coordinated lattice sites (the b site, which is slightly trigonally compressed octahedrally coordinated, and the d site, which is highly distorted octahedrally coordinated; there are three times as many d sites as b sites in the crystal) and only one anion site showing a tetrahedral coordination. The possible anion interstitial sites are 8a, 16c, and 24d in Wyckoff's notation, which all feature 6-fold coordination by oxygen. Our calculations as presented in Table 7 show that both anion and cation interstitials have lower energies in the 16c site. On relaxation, the anionic interstitial changes its coordination from octahedral to tetrahedral with the nearest lattice oxygen ions moving substantially outwards (by 0.349 Å) and the nearest cations inwards (by 0.126 Å for site b and by 0.339 Å for site d). Compared to previous calculations, we predict a substantially lower energy of oxygen at interstitial sites in In2O3 by ~5.0 eV compared to Warschikow and by ~1.2 eV compared to Walsh et al. This big difference, in particular from the former report, can perhaps be attributed to an incomplete relaxation of the lattice around the interstitial site (possibly, due to an appearance of a small barrier for the movement of next nearest neighbours with some sets of interatomic potentials).

The oxygen vacancy energies are 26.64 eV and 22.59 eV for SnO2 and In2O3, respectively, based on a more accurate simulation using a hybrid quantum mechanical/molecular mechanical (QM/MM) approach.25 (Note that there is uncertainty in these values as they require a value for the second electron affinity of O, as discussed above if we are to make direct comparison with Mott–Littleton values.) Our calculated values of 24.02 eV and 23.16 eV for SnO2 and In2O3, respectively, are much closer to the DFT based estimates than those from previous atomistic simulations that predicted 19.39 eV for SnO232 and 20.99 eV for In2O3.22

### 3.4. Oxygen vacancy formation

The loss of oxygen from the lattice can be represented in the Kröger–Vink notation as

$$\text{O}_\text{O}^\circ \rightarrow \text{V}_\text{O}^{\bullet} + \frac{1}{2} \text{O}_2(g) + 2e^\circ,$$  

(3.1)
Here the reaction is assumed to occur in an environment containing an excess of O$_2$(g), which is often referred to as “O-rich conditions” but corresponds approximately to the sample of interest being in air under ambient conditions. The neutral oxygen vacancy generated in the first step will provide two free electrons on ionisation. The energetics of this reduction process is

$$E = E[V_0^{••}] - A_O^{1-2} - \frac{1}{2}D_{O_2} + 2E_e,$$  (3.2)

where $E[V_0^{••}]$ is the oxygen vacancy defect energy, $D_{O_2}$ is the oxygen molecule dissociation energy (5.136 eV$^{48}$), $A_O^{1-2}$ is the sum of the first and second electron affinities of oxygen, and $E_e$ is the energy of introducing an electron into the conduction band from the vacuum (electron affinity of the material). This description is valid for any oxide material. Alternatively, when the oxygen partial pressure is low, so that the sample of interest is under strongly reducing conditions (”O-poor conditions”), oxygen vacancy creation in SnO$_2$ proceeds as:

$$O_2^• + \frac{1}{2}Sn(s) \rightarrow V_0^{••} + \frac{1}{2}SnO_2(s) + 2e^•,$$  (3.3)

while the defect formation energy can be written as

$$E = E[V_0^{••}] + \frac{1}{2}\Delta H^0(\text{SnO}_2) - \frac{1}{2}D_{O_2} + 2E_e - A_O^{1-2}.$$  (3.4)

where $\Delta H^0(\text{SnO}_2)$ is the standard enthalpy of formation of SnO$_2$.

The calculated oxygen vacancy formation energies of SnO$_2$ are 3.40 eV under O-rich/Sn-poor conditions and 0.36 eV under O-poor/Sn-rich conditions. Freeman and Catlow$^{12}$ reported 3.65 eV for the O-rich conditions. If we include the correction discussed above their formation energy would shift down to 1.55 eV, significantly lower than our result. Using periodic $ab$ initio models with the PBE0 exchange and correlation density functional, Scanlon et al.$^5$ have reported the corresponding doubly charged oxygen vacancy formation energy to be 6 eV under O-rich, and 3.4 eV under O-poor conditions (extracted from Fig. 2 of ref. 5), which is somewhat different from the result of Agoston et al.$^7$ who using the same density functional have reported the value of about 2.9 eV under O-poor conditions. More recently, Buckeridge et al.$^{25}$ have used hybrid QM/MM embedded-cluster calculations, and have obtained with a meta-GGA hybrid BB1K exchange and correlation functional the values of 5.24 eV under O-rich and 2.20 eV under O-poor conditions. The energies of defect formation from the latter study are of course shifted from those in our study by the same amount as that reported above for the defect energies (the difference being due to the change in the reference point). Thus, our values are still underestimated by about 1.8 eV – again an improvement in the older work.

Direct comparisons of our results with experiment are difficult to make, which is why we judge the accuracy of our method by comparison with other theoretical studies. We cannot derive defect transition levels, which are the most common properties used for comparison with experiment. The measured heat of reduction of SnO$_2$ under atmospheric conditions, which should be comparable to O-rich conditions, is 4.09 eV.$^{19}$ This value should be compared with the formation energy of the oxygen vacancy in the neutral charge state, which unfortunately we cannot simulate accurately using the Born model and Mott–Littleton approach. We note that the density functional theory studies mentioned above do produce results that compare well with the experimental value.

For In$_2$O$_3$, the formation of the oxygen vacancy under In-rich/O-poor conditions can be described as:

$$O_2^• + \frac{2}{3}ln(s) \rightarrow V_0^{••} + \frac{1}{3}ln_2O_3(s) + 2e^•,$$  (3.5)

and the oxygen vacancy formation energy is:

$$E = E[V_0^{••}] + \frac{1}{3}\Delta H^0(\text{In}_2\text{O}_3) - \frac{1}{2}D_{O_2} + 2E_e - A_O^{1-2}.$$  (3.6)

We obtain the energies of 2.76 eV under O-rich/In-poor conditions and −0.49 eV under O-poor/In-rich conditions for In$_2$O$_3$. Compared with SnO$_2$, the results are in a similar correspondence with embedded-cluster based calculations by Buckeridge et al. (2.45 eV under O-rich and −0.75 eV under O-poor conditions using BB1k).$^{25}$ Agoston et al.$^7$ have reported the oxygen vacancy formation energy of 1.2 eV under O-poor conditions using a hybrid HSE06 exchange and correlation functional.

We note that the calculations of defect formation energies, such as those presented in this section, are routinely determined using electronic structure techniques such as DFT. Moreover, such approaches should give results that are more accurate than those obtained using classical models. While possible for many cases involving point defects at the dilute limit, computing defect energetics using DFT (or beyond) for larger scale systems such as solid solutions, extended surfaces, interfaces or grain boundaries and materials containing line defects becomes intractable. We have demonstrated that our interatomic potential model can give defect formation energies comparable with those obtained using DFT. We can therefore conclude that the approach will be suitable to study defects in extended systems, as the lower computational load offers significant advantages over most electronic structure techniques. Such studies will be reported in future work. We now further validate our method by studying intrinsic disorder in more detail, and by analysing tin substitution and complex formation in ITO.

3.5. Frenkel and Schottky defects

Based on the calculated point defect formation energy (Tables 4 and 5) and the calculated lattice energy ($E[SnO_2] = −122.32$ eV, $E[In_2O_3] = −150.01$ eV), we can predict the dominant mechanism of the intrinsic ionic disorder and defect formation. In Tables 8 and 9 we compare the relevant Frenkel and Schottky defects in SnO$_2$ and In$_2$O$_3$.

An ion that leaves its lattice site and occupies a non-interacting interstitial site will form a Frenkel defect pair.
3.6. Electron and hole reaction energies

ITO is a solid solution, in which Sn is doped into In$_2$O$_3$ at low concentrations, at which the electronic mechanism of charge compensation dominates,

$$\text{In}^+_\text{In} + \text{SnO}_2(\text{s}) \rightarrow \text{Sn}^+\text{In} + \frac{1}{2}\text{In}_2\text{O}_3(\text{s}) + \frac{1}{4}\text{O}_2(\text{g}) + e'. \quad (3.11)$$

The chemical potential of gaseous oxygen could shift the balance to favour the formation of interstitial oxygen instead:

$$\text{In}^+_\text{In} + \text{SnO}_2(\text{s}) \rightarrow \text{Sn}^+\text{In} + \frac{1}{2}\text{In}_2\text{O}_3(\text{s}) + \frac{1}{2}\text{O}_2''.' \quad (3.12)$$

Table 8 Defect formation energy in SnO$_2$

| Defect           | Present work | Freeman and Catlow$^{32}$ | Hines et al.$^{47}$ |
|------------------|--------------|---------------------------|---------------------|
| Anion Frenkel    | 6.33         | 5.54                      | 7.99                |
| Cation Frenkel   | 9.26         | 9.63                      |                     |
| Schottky         | 7.92         | 5.19                      | 11.32               |
| Anti Schottky    | 6.69         | 8.61                      |                     |

Table 9 Defect formation energy in In$_2$O$_3$

| Defect           | Present work | Walsh et al.$^{22}$ |
|------------------|--------------|---------------------|
| Anion Frenkel    | 3.67         | 3.19                |
| Cation Frenkel   | 7.00         | 6.85                |
| Schottky         | 6.16         | 4.44                |
| Anti-Schottky    | 3.83         | 4.87                |

The formation energies for anion and cation Frenkel defect pairs in SnO$_2$ are calculated as:

$$E_{\text{Anion Frenkel}} = E\left[\text{O}^+_\text{Sn}\right] + E\left[\text{V}^-\text{O}\right]. \quad (3.7)$$

$$E_{\text{Cation Frenkel}} = E\left[\text{V}^\text{***}\text{Sn}\right] + E\left[\text{Sn}^-\text{***}\right]. \quad (3.8)$$

For Schottky defects, one formula unit of the compound is removed, while for the anti-Schottky defect, one formula unit of the compound is added as a stoichiometric interstitial:

$$E_{\text{Schottky}} = E\left[\text{V}^\text{***}\text{Sn}\right] + 2E\left[\text{V}^\text{***}\text{O}\right] + E[\text{SnO}_2]. \quad (3.9)$$

$$E_{\text{Anti-Schottky}} = E\left[\text{Sn}^-\text{***}\right] + 2E\left[\text{O}^+_\text{Sn}\right] - E[\text{SnO}_2]. \quad (3.10)$$

According to the calculations, we find that the primary type of the intrinsic disorder is the anion Frenkel pair in SnO$_2$, which agrees with the prediction from two preceding atomistic studies of Freeman and Catlow$^{32}$ and Hines et al.$^{47}$ Based on the lowest-energy anion and cation interstitials and vacancies, a similar conclusion can be drawn on the dominance of the anion Frenkel pair in In$_2$O$_3$. We note that the energies of the intrinsic disorder reactions in SnO$_2$ are high indicating that there will be very low levels of thermally generated defects. The Frenkel energies in In$_2$O$_3$ are somewhat lower.

Table 10 Reaction energies ($\Delta E_r$ in eV) for processes, in which electron and hole carriers are charge compensated by ionic defects

| Material     | O-Rich conditions | $\Delta E_r$ | O-Poor conditions | $\Delta E_r$ |
|--------------|-------------------|-------------|------------------|-------------|
| SnO$_2$      |                   |             |                   |             |
| Holes        |                   |             |                   |             |
| Electrons    | $h^+ + \frac{1}{2}\text{O}_2^+ + \frac{1}{3}\text{V}^-\text{O} + \frac{1}{4}\text{O}_2$ | $-1.90$     | $h^+ + \frac{1}{2}\text{O}_2^+ + \frac{1}{3}\text{In}^+ + \frac{1}{4}\text{SnO}_2$ | $-3.42$     |
|              |                   | $e^+ + \frac{1}{4}\text{O}_2(\text{g}) + \frac{1}{2}\text{O}^+_\text{In}$ | $4.50$      | $e^+ + \frac{1}{4}\text{Sn}^+\text{Sn} + \frac{1}{4}\text{V}^-\text{In}^++ \frac{1}{4}\text{In}_2\text{O}_3$ | $5.48$      |
| In$_2$O$_3$  |                   |             |                   |             |
| Holes        |                   |             |                   |             |
| Electrons    | $h^+ + \frac{1}{2}\text{O}_2^+ + \frac{1}{3}\text{V}^-\text{O} + \frac{1}{4}\text{O}_2$ | $-1.32$     | $h^+ + \frac{1}{2}\text{O}_2^+ + \frac{1}{3}\text{In}^+ + \frac{1}{6}\text{In}_2\text{O}_3$ | $-2.95$     |
|              |                   | $e^+ + \frac{1}{4}\text{O}_2(\text{g}) + \frac{1}{2}\text{O}^+_\text{In}$ | $2.29$      | $e^+ + \frac{1}{3}\text{In}^+\text{Sn} - \frac{1}{3}\text{V}^-\text{In}^+ + \frac{1}{3}\text{In}_2\text{O}_3$ | $5.12$      |

3.7. Doping and defect cluster formation in In$_2$O$_3$

To understand the balance of point defects and charge carriers in ITO in more detail, we will first consider the limit of infinite...
dilution where a Sn ion can occupy two cationic lattice sites 8b and 24d, in Wyckoff’s notation, and three interstitial sites including 8a, 16c (a lattice O site in the fluorite structure) and 24d. The corresponding reactions (3.11) and (3.12) for Sn substituting on the cationic sites are presented above. Alternatively, we can consider Sn stabilising on interstitial sites in In2O3. Our calculation shows that, as with intrinsic interstitial defects, interstitial tin also has a lower energy in the 16c site. These interstitial impurities can be compensated by oxygen interstitials according to (assuming O-rich conditions):

\[ V^+_i (\text{In}_2\text{O}_3) + \text{SnO}_{2i(\text{s})} \rightarrow \text{Sn}_i^{***} + 2\text{O}_i^{**}, \quad (3.14) \]

or compensated by electron carriers:

\[ V^+_i (\text{In}_2\text{O}_3) + \text{SnO}_{2i(\text{s})} \rightarrow \text{Sn}_i^{***} + 4e^- + \text{O}_2. \quad (3.15) \]

The energies of these reactions are, however, high (12.08 eV and 2.94 eV, respectively) (see Table 11 for the relevant defect energies), which should be compared with 0.05 and −2.24 eV for reactions (3.12) and (3.11). We, therefore, confirm that substitutional incorporation of Sn in In2O3 is much more favourable than interstitial incorporation, but in both cases compensation by electron carriers will dominate.

A preference for the substitutional site has also been seen experimentally, but, intriguingly a study using Mössbauer spectroscopy24 indicated that tin atoms tend to substitute for indium at the b-site rather than the d-site, despite there being three times more d than b sites. Our calculations show that the point defect energy of Sn\textsuperscript{+\textsubscript{i}}\textsubscript{In(b)} is only 0.01 eV lower than that of Sn\textsuperscript{+\textsubscript{i}}\textsubscript{In(d)}. Although the energy ordering we obtain is compatible with experiment, the difference is so small that it cannot be the source of the observed higher b-site occupation.

Next, we consider the formation of defect clusters involving Sn impurities in In2O3, which, while possibly affecting the performance of ITO in technological applications, may also change the balance in the relative energies of substitutional vs. interstitial incorporation and, furthermore, the dominant compensation mechanism. Our results so far indicate that electron compensation is most likely, but of the possible ionic compensation species, the most probable for both substitutional and interstitial Sn under oxygen rich conditions would be an interstitial oxygen. We recall that the interstitial oxygen in In2O3 is tetrahedrally coordinated by four cations, with one b-site (\(\frac{1}{4}, \frac{1}{4}, \frac{1}{2}\)) cation and three d-site (\(x, 0, \frac{1}{2}\)) cations, as shown in Fig. 3. The next-nearest-neighbour cationic sites around the interstitial oxygen are three b sites and nine d sites. We will consider defect clustering within the first and second coordination shells of the interstitial oxygen.

The binding energy of a cluster is calculated as the energy of the cluster minus the energies of the isolated species comprising that cluster. The resulting defect binding energies of clusters involving Sn and O interstitial complexes, including up to three interstitial O, are given in Table 11, while those involving substitutional Sn, with a ratio of up to four Sn to one O are listed in Table 12. For each cluster type of different Sn:O stoichiometry, only the most stable combinations are given. Following the notation used by Warschkow et al.,23 we use the symbol “·” to represent the first cationic shell and “···” for the second cationic shell. From the results in Table 11, we see that forming clusters between interstitial Sn and O lowers the energy significantly. We note, however, that, combining the energies of reactions (3.15) and twice that of (3.13) and the binding energy of the complex involving one interstitial O, the formation energy of the double donor complex is 3.71 eV, a considerable reduction over that of reaction (3.14), which compensates the interstitial Sn by two interstitial O, but still much higher than the energies of the reactions involving substitutional Sn formation. Clusters involving more O interstitials result in even higher formation energies, indicating that, while cluster formation does lower the energy for the incorporation of interstitial Sn, substitutional Sn will remain in the lower energy solution mode.

For clusters of nearest-neighbour Sn\textsuperscript{+\textsubscript{i}}\textsubscript{In} and O\textsuperscript{−\textsubscript{i}}, the results show that substitutional tin has a lower energy in the d cation site over the b site. When substituting the same number of indium ions, the binding energies of clusters which contain Sn\textsuperscript{+\textsubscript{i}}\textsubscript{In(d)} are at least 0.4 eV lower than the energies of clusters only including Sn\textsuperscript{+\textsubscript{i}}\textsubscript{In(b)}. Clustering of Sn proves to be stabilising from one to four substitutional Sn with binding energies of −1.54, −1.32, −1.10 and −0.78 eV per Sn ion.
Table 12  Sn$_{ni}$ and O$_i$ complex binding energies in In$_2$O$_3$. We compare our results with those of Warschkow et al.$^{23}$

| Sn : O$_i$ ratio | Defect cluster | Present work | Warschkow et al.$^{23}$ |
|-----------------|----------------|--------------|-----------------------|
| 1 : 1 [Sn$_{ni}$O$_i$]$^+$ | [Sn$_{ni(d)}$O$_i$]$^+$ | −1.54 | −1.29 |
| | (Sn$_{ni(b)}$O$_i$)$^+$ | −1.19 | −0.89 |
| | (Sn$_{ni(d)}$O$_i$)$^+$ | −0.93 | −1.16 |
| | (Sn$_{ni(b)}$O$_i$)$^+$ | −0.85 | −1.10 |
| 2 : 1 [2Sn$_{ni}$O$_i$]$^+$ | (2Sn$_{ni(d)}$O$_i$)$^{2+}$ | −2.64 | −1.91 |
| | (Sn$_{ni(b)}$Sn$_{ni(d)}$O$_i$)$^+$ | −2.26 | −1.54 |
| | (Sn$_{ni(b)}$Sn$_{ni(d)}$O$_i$)$^+$ | −2.23 | −2.09 |
| | (Sn$_{ni(b)}$Sn$_{ni(d)}$O$_i$)$^+$ | −2.15 | −2.05 |
| | (Sn$_{ni(b)}$Sn$_{ni(d)}$O$_i$)$^+$ | −1.74 | −1.54 |
| | (Sn$_{ni(b)}$Sn$_{ni(d)}$O$_i$)$^+$ | −1.73 | −1.63 |
| | (2Sn$_{ni(d)}$O$_i$)$^+$ | −1.66 | −2.08 |
| | (Sn$_{ni(b)}$Sn$_{ni(d)}$O$_i$)$^+$ | −1.58 | −2.00 |
| | (2Sn$_{ni(d)}$O$_i$)$^+$ | −1.50 | −1.97 |
| 3 : 1 [3Sn$_{ni}$O$_i$]$^*$ | (3Sn$_{ni(d)}$O$_i$)$^*$ | −3.31 | −1.86 |
| | (Sn$_{ni(b)}$2Sn$_{ni(d)}$O$_i$)$^*$ | −2.90 | −1.49 |
| | (Sn$_{ni(b)}$2Sn$_{ni(d)}$O$_i$)$^*$ | −2.89 | −2.14 |
| | (2Sn$_{ni(b)}$Sn$_{ni(d)}$O$_i$)$^*$ | −2.55 | −2.35 |
| | (2Sn$_{ni(d)}$Sn$_{ni(d)}$O$_i$)$^*$ | −2.44 | −2.31 |
| | (2Sn$_{ni(d)}$Sn$_{ni(d)}$O$_i$)$^*$ | −2.37 | −2.24 |
| | (3Sn$_{ni(b)}$O$_i$)$^*$ | −2.18 | −2.55 |
| | (2Sn$_{ni(b)}$Sn$_{ni(d)}$O$_i$)$^*$ | −2.01 | −2.43 |
| | (2Sn$_{ni(d)}$Sn$_{ni(d)}$O$_i$)$^*$ | −1.96 | −1.88 |
| | (2Sn$_{ni(d)}$Sn$_{ni(d)}$O$_i$)$^*$ | −1.85 | −2.36 |
| | (3Sn$_{ni(b)}$O$_i$)$^*$ | −1.83 | −2.33 |
| 4 : 1 [4Sn$_{ni}$O$_i$]$^{**}$ | (Sn$_{ni(b)}$3Sn$_{ni(d)}$O$_i$)$^{**}$ | −3.12 | −0.88 |

After taking into account the next-nearest-neighbour shell, we find a much lower energy for the tin substituting for indium at d sites within the first coordination shell of the O interstitial forming (Sn$_{ni(d)}$O$_i$),$^+$ (2Sn$_{ni(d)}$O$_i$)$^{+}$ and (3Sn$_{ni(d)}$O$_i$)$^{+}$. As the latter proves to be most energetically favoured, we conclude that single electron donor complexes will donate electron charge carriers under thermodynamic equilibrium with up to three impurities per one electron. Therefore, a strategy to make doping more effective would require preventing Sn ions from clustering under oxygen poor conditions. Our prediction of the Sn dominant occupation of d sites on the cationic sublattice corroborates the report of Warschkow et al.$^{23}$ who also found a strong d-site preference.

Considering defect formation energies of complexes between substitutional Sn and interstitial O$_i$, we should account for all involved reactants as shown in eqn (3.16)–(3.19):

$$\text{In}^+_\text{In} + \frac{1}{4} O_{2(g)} + e^- + \text{SnO}_2(s) \rightarrow [\text{Sn}^*_\text{InO}] + \frac{1}{2} \text{In}_2\text{O}_3(s),$$

(3.16)

$$\text{In}^+_\text{In} + \text{SnO}_2(s) \rightarrow \frac{1}{2} [2\text{Sn}^*_\text{InO}] + \frac{1}{2} \text{In}_2\text{O}_3(s),$$

(3.17)

$$\text{In}^+_\text{In} + \frac{1}{3} [3\text{Sn}^*_\text{InO}] + \frac{1}{2} \text{In}_2\text{O}_3(s) + \frac{1}{12} O_{2(g)} + \frac{1}{2} e^-,$$

(3.18)

$$\text{In}^+_\text{In} + \text{SnO}_2(s) \rightarrow \frac{1}{4} [4\text{Sn}^*_\text{InO}] + \frac{1}{2} \text{In}_2\text{O}_3(s) + \frac{1}{8} O_{2(g)} + \frac{1}{2} e^-.$$  

(3.19)

The calculated reaction energies allow us to compare the stability of Sn in different complexes with elementary substitutional sites. We obtain 1.14, −0.69, −1.80 and −1.87 eV for the respective reactions, which are, however, still above the Sn$_{ni}$ energy of formation of −2.24 eV. From these observations we conclude that electronic rather than oxygen interstitial compensation will dominate in Sn doped In$_2$O$_3$, but that any available interstitial O$_i$ will be complexed with Sn.

4. Conclusions

We have developed a new set of transferable pairwise interatomic potentials for SnO$_2$ and In$_2$O$_3$. The new potentials offer an improvement over the previously available models, in particular for the lattice and defect properties, and give defect formation energies comparable with those obtained using DFT. Using the newly developed potentials, we have investigated isolated intrinsic defects along with electron and hole formation; Sn impurities in In$_2$O$_3$, and effects of impurity clustering, and their thermodynamic stability. Our calculations show a significant improvement – compared to older parameterisations that can be found in the literature – of lattice energies and oxygen vacancy formation energies of both SnO$_2$ and In$_2$O$_3$ that are in acceptable agreement with experiment and available QM/MM results.$^{25}$ The study of intrinsic defects reveals a lower energy for the formation of anion Frenkel pairs in both binary oxide materials, which, however, have higher energies than the formation energy of positively charged oxygen vacancies compensated by electrons and with oxygen loss. We show unambiguously the dominant electronic compensation mechanism stabilising Sn impurities at cation substitutional sites in In$_2$O$_3$. The study of impurity clustering with interstitial oxygen reveals a progressive stabilisation of Sn on cluster growth, which points to an increasing role of the ionic charge compensation with the level of doping in In$_2$O$_3$. Work is in progress on modelling ITO at finite levels of doping, results of which will be reported in the near future.

Conflicts of interest

There are no conflicts to declare.

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