Theory of Defects in *n*-Type

Transparent Conducting Oxides

Qing Hou

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Supervised by Professor C. Richard A. Catlow

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Department of Chemistry

20 Gordon Street

London WC1H 0AJ

United Kingdom

Declaration

I, Qing Hou, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

Abstract

A range of computational modelling techniques are employed to explore the structures, defect and electronic properties of three transparent conducting oxides (TCOs): SnO₂, In₂O₃ and ZnO.

Bulk interatomic potential (IP) based calculations are carried out to model point defects in SnO₂ and In₂O₃. We report new IPs for the two binary oxides, which offer an improvement over the previously available models, and give defect formation energies comparable with those obtained using density functional theory (DFT).

The intrinsic point defects in ZnO are investigated in detail using a hybrid quantum mechanical/molecular mechanical (QM/MM) embedded cluster approach. The formation energies show the oxygen vacancy to be the most favourable under O-poor conditions and zinc vacancies under O-rich conditions. Our calculations are also able to assign several of the widely studied luminescence bands to defect states.

For extrinsic dopants, including in ZnO, we compute the structure and formation energies of Li and H dopants in both substitutional and interstitial form and their complexes, the Li_{Zn}-Li_{i(oct)} complex has the lowest formation energy in Zn-poor conditions. The H_O is energetically favoured compared to H_i.

Using QM/MM calculations, we investigate the native point defect on the electrical and optical properties of In_2O_3 . The oxygen vacancy is the lowest-energy donor defect, with a predicted luminescence peak at 2.12 eV using the B97-2 functional.

Finally, we study the solid-solution of In_2O_3 and SnO_2 over a range of dopant concentrations, which provide local structure information.

Impact Statement

The growing demand for TCO materials has stimulated a large amount of research on these materials over the past half century. Nevertheless, many key basic properties of TCOs are still controversial. Computational techniques can make a unique contribution to our understanding of the defect chemistry, electronic properties and luminescent behaviour of the most intensively studied TCOs (SnO₂, In₂O₃ and ZnO), which control many of the applications of the materials.

The benefit of this work is the insight it has provided into the defect structures and processes in TCOs, contributing extensive new knowledge and data on this class of material of direct interest to our colleagues in the materials, physical and chemical theory and simulations communities. The new approaches and methods we have developed can provide effective solutions to a range of problems, which will help computational scientists who encounter similar challenges. Our work will help experimentalists interpret their data and provide them with new pointers leading to developing and performing new experiments, leading to new discoveries in the field. Additionally, the technological and engineering communities will be able to apply the new fundamental knowledge to understand better and to optimise current materials and devices and then design new ones, leading to the targeted materials design and development of new types of devices and processes.

TCOs with high optical transparency and high electrical conductivity are used widely in bulk chemical, electronics, machinery, energy, building and construction, pharmaceutical, food and other industries contributing to everyone's daily lives. The impact of this work will be directly or indirectly on the life of ordinary people globally, and we anticipate that the new knowledge will in due course permeate into the curricula for physics and chemistry and materials science in undergraduate and postgraduate university courses.

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List of Abbreviations

TCO	transparent conducting oxide
IP	interatomic potential
DFT	density functional theory
LDA	density approximation
GGA	generalised gradient approximation
PL	photoluminescence
HCP	hexagonal close-packed
CL	cathodoluminescence spectroscopy
PC	photoconductivity
ODMR	optically detected magnetic resonance
GL	green luminescence
DLTS	deep level transient spectroscopy
EPR	electron paramagnetic resonance
YL	yellow luminescence
RL	red luminescence
OL	orange luminescence
QM	quantum mechanical
HF	Hartree-Fock
SCF	self-consistent field
ECP	effective core potential
QM/MM	quantum mechanical/molecular mechanical
GULP	General Utility Lattice Program
CBM	conduction band minimum
СВ	conduction band
VBM	valence band maximum
VB	valence band
ZPL	zero-phonon line

List of Abbreviations

- KLMC Knowledge Led Master Code
- LAMMPS Large-scale Atomic/Molecular Massively Parallel Simulator
- HPC High Performance Computing
- ITO indium tin oxide
- CC configurational coordinate
- FTIR-PC Fourier transform infrared photocurrent
- PLD pulsed-laser deposition
- DAP donor-acceptor pair
- PAS positron annihilation spectroscopy
- sX screened exchange
- HDF hybrid density functional
- ESR electron spin resonance
- BC body centred
- AB antibonding
- LSDF Local-spin-density-functional
- EPMA electron probe microanalyzer
- XRD x-ray diffraction

Chapter 1

Introduction

1.1 Background and Motivation

Generally, conductivity and optical transparency are incompatible because transparency requires band gaps larger than 3.3 eV which makes carrier doping very difficult. 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.

TCO materials can be used as transparent electrodes in liquid crystal displays (LCD) [1], which can be the positive and negative electrodes together with liquid crystal electrodes, to drive the rotation of liquid crystal molecules to present different characters and images. In addition to LCD, TCOs are widely used in transparent electrodes for flat panel displays [2], solar cells [3, 4], light emitting displays (LED) [5], Organic light emitting displays (OLED) [6, 7], antistatic coating [8], heat reflecting filters [9], infrared reflective coating [10], electrochromic devices and smart windows [11] and transparent thin films transistors [12]. The growing demand for this kind of material has, therefore, resulted in extensive research on TCO materials over the past half century.

The applications of TCOs depends critically on the band structure of the material. By doping to increase the free carrier density sufficiently to move the Fermi level into the conduction band, the oxide can be made electronically degenerate. Degenerate doping needs point defects or impurities with an ionization energy close to the conduction band to donate electrons. For TCO materials such as the most commonly used SnO₂, In₂O₃ and ZnO, there are,

however, still many topics that remain controversial in the study of their defect properties.

ZnO exhibits strong *n*-type conductivity with electrons in the conduction band as charge carriers. Despite extensive research, the source of this conductivity is still a matter of debate. For many years, the *n*-type conductivity has traditionally been attributed to intrinsic defects. However, in 2000, a firstprinciple density functional calculations carried out by Van de Walle revealed that none of the native defects exhibits characteristics consistent with a highconcentration shallow donor, but that hydrogen is an excellent candidate to incorporate in high concentrations and behaves as a shallow donor. [13] The source of the *n*-type conductivity of SnO₂ and In₂O₃ also remain a topic of debate. The *n*-type conductivity has intuitively been attributed to the presence of oxygen vacancies, but other sources have also been proposed. [14-17]

A second widely investigated aspect of these materials is their luminescent properties. More generally, the origin of luminescent transitions has long been one of main research topics for luminescent materials and for more than half a century, extensive research has been devoted to the luminescence properties of TCO materials, including both intrinsic and extrinsic luminescence. However, the exact origin of the intrinsic luminescence due to native defects is still controversial but is related to its electronic and defect properties.

The main aim of this work is therefore to understand the defect chemistry, electronic properties and luminescent behaviour of the *n*-type TCO materials, to achieve which we use a range of computational modelling approaches based both on interatomic potential and electronic structure techniques.

1.2 Thesis Outline

The work of this thesis focuses on the three most commonly used *n*-type TCO materials: SnO_2 , In_2O_3 and ZnO. In Chapter 4, we present a consistent interatomic force field for indium sesquioxide (In_2O_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. In Chapter 5, intrinsic point defects in ZnO are investigated using hybrid quantum

1.2 Thesis Outline

mechanical/molecular mechanical (QM/MM) embedded cluster approach. We have studied the structure, formation and ionisation energies, and the equilibrium defect and carrier concentrations of the point defects. In Chapter 6, we report the properties of Li and H in both substitutional and interstitial form and their complexes, which again are investigated using the QM/MM embedded cluster approach. Chapter 7 contains the study of intrinsic point defects in In₂O₃ using the QM/MM embedded cluster approach, while in Chapter 8, the solid solutions of In₂O₃ and SnO₂ are investigated using the interatomic potential model derived in Chapter 4.

The following chapter summarises the relevant background and literature and Chapter 3 then describes the computational methodologies employed.

Chapter 2

Literature review

2.1 Indium Oxide

Indium sesquioxide (In_2O_3) is an *n*-type semiconductor, and it is generally thought that both the intrinsic oxygen vacancies and the extrinsic dopants, especially Sn, contribute to the carrier concentration. [18] Indeed Sn doped In_2O_3 (referred to as ITO) is a widely studied material. After Rupprecht [19] first carried out the study on the optical and electrical properties of In_2O_3 in 1950s, In_2O_3 and ITO have attracted considerable experimental and theoretical interest.

2.1.1 Crystal and Defect Sites

At low temperature and ambient pressure, In_2O_3 adopts the body-centred cubic bixbyite crystal structure (space group No. 206, Ia3, a=10.117 Å), which contains 80 atoms or 16 formula units in its conventional cubic unit cell. The structure can be viewed as a 2 ×2 ×2 supercell of the fluorite (CaF₂) lattice with one quarter of the anionic sites vacant, which results in two types of cationic sites, 8*b* and 24*d* in Wyckoff's notation, as illustrated in Figure 2.1. These structural vacant sites (Wyckoff 16*c*) can provide spaces for oxygen as interstitials. Both structural oxygen and vacant sites are coordinated by four cations, one *b* site, and three *d* sites.



Figure 2.1 Lattice sites in In_2O_3 . In the right hand figure, the coordination of the cations is shown, with In ions represented by the larger purple spheres and O ions by the smaller red spheres.

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. Frank and Köstlin [20] reported a defect model that includes two kinds of interstitial oxygen: one is loosely bound to tin, the other forming a strongly bound Sn₂O₄ complex. Subsequently, the structural property of the defect cluster with substitutional tin and interstitial oxygen has been extensively modelled by Warschkow *et al.*. [21, 22]

The interstitial oxygen in \ln_2O_3 is tetrahedrally coordinated by four cations, with one *b*-site cation at x=y=z=1/4 on the 16*c* axis and three *d*-site cations, as shown in Figure 2.2. The ideal position of the interstitial oxygen should be equidistant from the four cations, which is x=y=z=0.116. González *et al.* [23] reported the interstitial position to be x=y=z=0.086 in bulk-ITO samples and x=y=z=0.091 in nano-ITO samples by experiment. Mössbauer experimental results suggested that the tin atoms substitute to the *b*-site indium rather the *d*site indium. [24] However, density functional calculation results suggested that only when Sn dopants are located at the *d*-site nearest to the oxygen interstitial, can displacement of interstitial oxygen from the ideal fourfold position be plausible. [21]



Figure 2.2 Interstitial oxygen position in In₂O₃.

2.1.2 Defects in In₂O₃

The material properties of In_2O_3 , including the electronic properties, are dependent on the defect chemistry and it is, therefore, essential to understand the defect properties of In_2O_3 .

Regarding theoretical investigations, there have two classes of computational technique that have been used to study point defects in In₂O₃: interatomic potential methods and density functional theory (DFT).

Using interatomic potential methods, Warschkow *et al.* [21, 22] determined the local geometry and energetics of defect clusters containing one to three tin dopant substitutional atoms around a single oxygen interstitial in In₂O₃. They found a strong *d*-site preference in nearest coordination to an interstitial. Walsh *et al.* [25] have reported an accurate interatomic potential for indium oxide. Moreover, the formation of intrinsic defects calculated using the Mott-Littleton approach shows anion Frenkel pairs to be the lowest energy form as a result of the structural anion vacancy sites in the bixbyite structure. They then investigated further the thermodynamics of anion Frenkel pair formation and found that the anion Frenkel pairs are likely to contribute to the high-temperature thermal expansion of In₂O₃. [26]

Using local density approximation (LDA) and a LDA + U approach in DFT, Reunchan and co-workers [27] proposed that the oxygen vacancy is a double donor, while the indium vacancy is a triple acceptor in indium oxide; while

2.1 Indium Oxide

Agoston et al. [28] investigated electron compensation in In₂O₃ using hybrid functional HSE06 and found that *n*-type doping is intrinsically limited by compensating acceptor defects in In₂O₃. Using the generalised gradient approximation (GGA), Lany and Zunger [29] calculated the defect and carrier densities in In₂O₃. They found that oxygen interstitials are remarkably unstable, oxygen vacancies and indium interstitials do not lead to more than 10¹⁴ cm⁻³ free electrons at room temperature in equilibrium, which fails to explain the observed electron densities of 10¹⁸ cm⁻³. In contrast, intrinsic defects are observed to have an effect on the band structure and the optical properties. LDA calculations by Palandage and Fernando [30] show that the indium interstitial coexisting with an oxygen vacancy is a good candidate to create donor levels in the gap region of In₂O₃, contributing to the free electron density and hence conductivity. Huang et al. [31] reported that the oxygen vacancy and indium interstitial are close to the bottom of conduction band and act as shallow donors, while the defect energy states of the indium vacancy and oxygen interstitial are just above the top of the valence band and act as shallow acceptors using the GGA method. Contrary to this, first-principles molecular orbital calculations [32] suggested that the oxygen vacancy cannot act as a native donor because the defect level formed is much lower than the conduction band bottom. The native donor in In_2O_3 was proposed to be an indium interstitial which can generate a shallow donor level, but with the coexistence of an oxygen vacancy.

Experimentally, Rosenberg [33, 34] found a consistent statistical interpretation assuming the predominant defect in In_2O_3 is the interstitial indium by the oxidation rate measurement, which was later accepted by De Wit [35] using Hall and conductivity measurements.

2.2 Tin Oxide

2.2.1 Crystal Structures

Tin dioxide (SnO₂) is an intrinsic, *n*-type semiconductor which crystallizes in the tetragonal rutile structure (space group No. 136, P4₂/mnm, a=4.737 Å, c=3.185 Å, *u*=0.307) [36] as shown in Figure 2.3. The rutile structure of SnO₂ has only one octahedrally coordinated lattice site for cations and one trigonal site for anion, which can be thought of as infinite columns of edge sharing SnO₆ octahedra; each edge-shared oxygen is corner shared with an adjacent infinite chain. Each tin is coordinated to six oxygen and each oxygen is coordinated to three tin, two within a column, and one within the adjacent column. There are two possible cationic interstitial sites in SnO₂, in Wyckoff 4*c* site (0, 0.5, 0) (green ball in Figure 2.3), which is in the centre of an unoccupied oxygen octahedron, and Wyckoff 4*g* site (*u*, -*u*, 0) (*u* being the variable parameter of the rutile structure, blue ball in Figure 2.3).



Figure 2.3 Crystal structure of bulk SnO₂. The coordination of the cations is shown, with Sn ions represented by the larger grey spheres, O ions by the smaller red spheres, 4c interstitial sites by green spheres and 4g interstitial sites by blue spheres.

2.2.2 Defects in SnO₂

A number of studies have been reported on aspects of the atomic structure, electronic structure and surface properties of SnO₂, as a result of the widespread applications of the material due to its unique properties. Intrinsic defects in SnO₂ are, moreover, thought to contribute to the conductivity, which can be further enhanced by extrinsic doping.

An early computational study on the defect and dopant properties was reported by Freeman and Catlow. [37] Based on the reported set of potentials, the Schottky and Frenkel defects are found to have similar energies with that of Schottky trio slightly lower, and the calculations predicted that a significant proportion of dopant species will be in interstitial sites. Using interatomic potential methods, Hines *et al.* [38] reported anion Frenkel is the most stable defect and the anion interstitial tend to occupy (0, 0.5, 0) site which in contrast the (u, -u, 0) reported by Freeman and Catlow. [37]

DFT studies of defects in SnO₂ have focused mainly on oxygen vacancies rather than considering a range of defects. Based on a tight-bind Green'sfunction calculation, the oxygen vacancy was reported to produce shallow donor levels [39], which was later predicted by LDA-DFT calculations [40]. They found that the tin interstitial and oxygen vacancy dominate in the defect structure of SnO₂ with surprisingly low formation energies and strong mutual attraction. In contrast, the LDA/LDA+U results reported by Janotti and van de Walle [41] show that the oxygen vacancy is a deep donor and the Sn interstitial is unstable with very high formation energy, the tin antisite has even higher formation energies and is also an unlikely source of conductivity in SnO₂. Buckeridge et al. [42] also observed the oxygen vacancy is a negative U deep donor using the hybrid functionals by QM/MM embedded cluster approach. Their results are in good agreement with the plane-wave supercell based study by Scanlon and Watson. [43] Godindho et al. [44] predicted oxygen vacancies compensated through Sn reduction to be the most abundant intrinsic defect under oxygen-poor conditions, in their GGA-DFT study on the electronic property of the most probable isolated defects and their clustered pairs.
Experimentally, oxygen vacancies, rather than tin interstitials, were found to be the cause of nonstoichiometry in SnO₂. By measuring the conductivity as a function of oxygen partial pressure at elevated temperatures using a four-point technique, Samson and Fonstad [45] found the dominant native defect in SnO₂ is a doubly ionisable oxygen vacancy.

2.2.3 Optical properties in SnO₂

Due to the high electrical conductivity and high optical transparency properties, SnO₂ can be used as a transparent conducting electrode in opto-electronic devices. The study of photoluminescence (PL) properties of SnO₂ is of significance for the optoelectronic integration of these devices.

The PL peak is usually due to the radiative recombination involving some defect states. Gu *et al.* [46] investigated the optical properties of SnO₂ particles synthesised by a simple sol-gel method. They assigned the luminescence to the recombination of electrons in a conduction band with holes in the oxygen vacancy centre. The experimental results by Luo *et al.* [47] showed that surface oxygen vacancies are the possible origin of the observed two emission peaks of the ultra-long SnO₂ nanowires synthesised by thermal oxidation of tin powder using gold film as the catalyst. Similarly, Jeong *et al.* [48] found that the peak of the SnO₂ thin films by thermal chemical vapor deposition at 2.4 eV was due to the concentrations of oxygen vacancies and another peak at 3.1 eV was related to structural defects.

2.3 Zinc Oxide

2.3.1 Crystal Structures

Zinc oxide is a transparent semiconductor with a direct band gap of 3.4 eV. Under ambient conditions, ZnO crystallizes in the wurtzite structure (space group P6₃mc, a=3.2495 Å, c=5.2069 Å) [49] as shown in Figure 2.4. The wurtzite structure of ZnO is composed of two interpenetrating hexagonal closepacked (HCP) sublattices, in which anion and cation tetrahedra are bonded to four corresponding hexahedra.



Figure 2.4 Crystal structure of bulk ZnO. The coordination of the cations is shown, with Zn ions represented by the larger grey spheres and O ions by the smaller red spheres, the colour scheme adopted in all following figures.

2.3.2 Intrinsic Defects in ZnO

Native defects play a key role in the electrical and optical properties of ZnO, such as controlling doping, luminescence efficiency and minority carrier lifetime. Therefore, understanding the intrinsic point defects in ZnO is important to its successful device application.

Experimentally, Hagemark and co-workers have carried out an extensive study on the ZnO defect system. [50-53] Two donors, a native donor zinc interstitial and an unknown donor D, and a native acceptor, zinc vacancy, have been suggested as the major defects. The unknown donor could be a frozen-in oxygen vacancy which thermodynamically cannot be distinguished from a foreign donor. Thomas [54] introduced zinc interstitials into zinc oxide by heating the crystals in zinc vapor followed by rapid quenching. Instead of forming oxygen vacancies, the zinc atmosphere produced zinc interstitials which were found to act as donors with a low ionisation energy. Look and Hemsky [55] also reported that the shallow donor level at about 30 meV below the conduction band minimum could be attributed to zinc interstitials; and the zinc interstitial (and not the oxygen vacancy) is the dominant residual native shallow donor in ZnO. However, later, theoretical calculations have suggested that the oxygen vacancy is a deep, not a shallow donor, and the H impurity is a better dominant shallow donor candidate.

Janotti and van de Walle performed a systematic study of the native defects in ZnO. [41, 56-59] Using LDA and LDA+U-DFT, they find that oxygen vacancies

are deep rather than shallow donors with high formation energies; zinc interstitials are shallow donors which also have high formation energies; zinc vacancies are deep acceptors and are probably related to the green luminescence; oxygen interstitials act as deep acceptors at octahedral site with high formation energies. The first principles study by Erhart et al. [60, 61] also showed that the oxygen vacancies are deep donors while the zinc interstitials are shallow donors. The oxygen dumbbell interstitials are shallow acceptors, while the zinc vacancy is the dominate acceptor under oxygen-rich conditions for Fermi levels in the upper half of the band gap. Oba et al. [62] reported that the oxygen vacancy induces a deep and localised in-gap state, whereas the zinc interstitial is a shallow donor and hence can be a source of the carriers. They proposed that the oxygen vacancy is relevant to the nonstoichiometry of ZnO, and that sources other than the native defects such as the H impurity need to be considered for the *n*-type conductivity. Vidya et al. [63] found the oxygen vacancy would be the dominant intrinsic defect under both Zn-rich and O-rich conditions and it is a deep double donor by density functional calculations. The zinc interstitial and zinc antisite were found to be shallow donors with formation energies higher than that of the oxygen vacancy.

2.3.3 Extrinsic Dopants in ZnO

In 1950s, Mollwo [64] and Thomas and Lander [65] reported that hydrogenation of ZnO at high temperatures produces *n*-type conductivity. However, little attention was focused on those results for many years until first-principle calculations predicted that hydrogen in ZnO is always present and acts as a donor. van de Walle [13] firstly reported that hydrogen acts as a source of conductivity, it can incorporate in high concentrations and behaves as a shallow donor. Hydrogen is tightly bound to an oxygen atom in ZnO forming an OH bond. Oba *et al.* [66] reported the H interstitial and substitutional as shallow donors that are likely to form with a substantial concentration in *n*-type ZnO. Lyons *et al.* [67] reported that the hydrogen forms highly stable complexes with the zinc vacancy with the acceptor levels closer to the VBM. The hydrogenated zinc vacancy.

Experimentally, Lavrov *et al.* [68] identified two shallow donors: hydrogen at the body-centred lattice site H_{BC} with an activation energy of 53 meV and hydrogen bound in an oxygen vacancy via a combined study of Raman scattering, IR absorption and photoluminescence. They then performed a Raman study and found that most hydrogen forms shallow donors H_{BC} . H_{BC} migrates through the crystal and forms electrically inactive H_2 . [69] The EPR and ENDOR studies at 95 GHz by Hofmann *et al.* [70] identified that one of the two observed donor resonances is related to hydrogen with a concentration of about 6*10¹⁶ cm⁻³. Shimomura *et al.* [71] reported a determination of the location of a muonium (Mu, an analogue of isolated hydrogen whose proton is substituted by a positive muon) as a shallow donor in ZnO. Cox *et al.* [72] also reported Mu in ZnO act as a shallow donor by direct spectroscopic observation of its muonium counterpart.

Depending on the growth method, nominally undoped ZnO single crystals may contain In, Ga, Al, Pb donors, Li acceptors, and a row of transition metal impurities (V, Mn, Cu, Co, Fe, Ni). [73, 74] Therefore, it is important to understand the effects of the each dopant.

Li is known to act as a major impurity in ZnO growth. However, the location of the acceptor level of Li substitutional Zn (Li_{Zn}) remains controversial. Firstprinciples calculations by Lee and Chang found that Li_{Zn} is a shallow acceptor while it is mostly compensated by Li interstitial (Li_i). However, when co-doped with H impurities, the formation of compensating interstitials is severely suppressed, and the acceptor solubility is greatly enhanced by forming H-acceptor complexes. [75, 76] Park *et al.* [77] also found that substitutional group-I elements are shallow acceptors. Experimental work using cathodoluminescence spectroscopy (CL), photoconductivity (PC) and Hall-effect measurements reported the acceptor state among 150 meV- 260meV. [78, 79]

In contrast, instead of introducing a shallow level, other calculations reported the Lizn to be a deep acceptor. Carvalho *et al.* found that the ionisation level of Lizn is between 0.6-1.1 eV above the valance band, which explains the difficulty in realising *p*-type ZnO using Li as monodopant. [80] Sokol *et al.* [81] reported

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the defect level of Li_{Zn} is at 0.807 eV above the valance band, which is in agreement with experiments. [82] The Li acceptor level is at least 500 meV above the valence band and optically detected magnetic resonance (ODMR) showed that radiative recombination occurs with the deep state. [83]

2.3.4 Optical properties in ZnO

There are numerous studies on the common luminescence bands observed in ZnO including green, yellow, orange and red broad bands, but the exact source of the intrinsic luminescence of ZnO due to native defects is still controversial.

Green luminescence (GL) centred at about 2.5 eV is the most commonly observed emission in ZnO. However, the nature of the GL has been one of the most controversial topics. Some studies assign the GL to the oxygen vacancy. Vanheusden and co-workers [84, 85] reported that the recombination of a photogenerated hole with the singly ionised charge states of oxygen vacancy is responsible for the GL in ZnO. The experimental results by Wu *et al.* [86] and Li *et al.* [87] also suggested the same mechanism. The photoluminescence (PL) and deep level transient spectroscopy (DLTS) result of Hofmann *et al.* [88] suggested a correlation between the GL at 2.45 eV and a donor level 530 meV below the conduction band, which was attributed to (0/++) transition (from 0 to +2 charge state) of the oxygen vacancy.

Some studies speculated that zinc vacancies contribute to the GL. Čížek *et al.* [89] found that the GL has multiple origins and consists of a band at 2.3 eV due to recombination of electrons of the conduction band by zinc vacancy acceptors coupled with hydrogen and a band at 2.47 eV related to oxygen vacancies. Heo *et al.* [90] assigned the GL to the transition from donor to deep zinc vacancy acceptors.

Kappers *et al.* [91] found that there is no correlation between the GL and the presence of oxygen and/or zinc vacancies, using optical absorption, PL and electron paramagnetic resonance (EPR) on ZnO grown by the seeded chemical vapor transport method. Other native defects have been proposed to be the origin of the green luminescence. For example, Korsunska *et al.* [92] suggested that the emitting centres responsible for GL are complex defect

including zinc interstitials, while Lin and Fu [93] concluded that the GL corresponded to the oxygen antisite defect.

Yellow luminescence (YL) is also commonly observed in ZnO which is less controversial. The YL is commonly associated with excess oxygen. Zelikin and Zhukovskii [94] attributed the YL to an excess of oxygen or Zn vacancies near extended lattice defects. Wu *et al.* [86] suggested that the mechanism responsible for the YL is the recombination of a delocalised electron close to the conduction band with a deeply trapped hole in the single negatively charged interstitial oxygen ion. Other hypotheses such as Li impurities [95, 96] or OH groups [97] also have been proposed.

Red luminescence (RL) and orange luminescence (OL) are less commonly observed in ZnO than GL and YL. RL and OL are commonly reported to correspond to the presence of excess oxygen. Studenikin *et al.* [98] found the GL and OL resulted from oxygen-poor and oxygen-rich conditions, respectively, in ZnO. Wu *et al.* [99] also observed the orange emission disappeared and GL appeared due to the deficient of oxygen in the reducing atmosphere. They attributed the orange emission to oxygen interstitials. Djurišić *et al.* [97] concluded that the RL is related to oxygen interstitials, but possibly involving zinc vacancy complexes.

2.4 Perspective

It is clear that despite extensive study over many years, both the defect structures and origins of luminescent bands in these materials remains uncertain and often controversial. This thesis aims to clarify the fundamental defect and luminescent properties of the materials using state-of-the art computational methods.

Chapter 3

Theoretical Methods

3.1 Introduction

Computational modelling methods are used to calculate structures and electronic properties of molecules and solids. Computational modelling is a particularly useful tool for the study of defects in solid-state systems, because of the difficulties in studying defects directly through experiment. In particular, calculations can be used to assist in the analysis and interpretation of experimental data.

Interatomic potential (IP) and quantum mechanical (QM) methods are two of the most widely used approaches in computational chemistry. The IP method provides a computationally less demanding approach to calculating structural and energetic properties, while the QM method, which is far more computationally intensive provides descriptions of the electronic structures, properties and reactivity. Therefore, according to different demands, different computational techniques need to be selected. The IP method can be used to investigate large systems and a large number of structural configurations in a relatively short computational time. The QM methods are suitable to model accurate electronic structures and properties.

In this chapter, a detailed overview of both the IP method and QM method used in this thesis is given. Firstly, a brief description of the theory of the IP and QM methods is given. We then describe the defect calculations methods using the two levels of theory. Finally, the details of the software packages used in this thesis are given.

3.2 Interatomic potential Methods

The interatomic potential method, (sometimes referred to as the atomistic method), is based on the use of function (or less commonly numerical) forms and parameter sets to calculate the potential energy of a system of atoms or ions as a function of their coordinates in static lattice and molecular dynamics simulations. The classic interatomic potential method allows calculations to be performed on structures containing many thousands of atoms in a relatively short computational time. However, atomistic simulations based on interatomic potentials neglect the quantum aspects of the nuclear and electronic degrees of freedom, so that the electron structures or electron state cannot be calculated directly. Nevertheless, they can reproduce well, cohesive, elastic and dielectric properties of solids and can be used to predict properties as a function of temperature.

3.2.1 Energy calculation

The internal energy of a solid is a function of the position and momentum of all electrons and nuclei, which is very complicated. The interatomic potential method simplifies this calculation by incorporating the effect of the electrons into a single atomic centre. The energy of the system can be determined by:

$$U = \sum_{i=1}^{N} U_i + \frac{1}{2!} \sum_{i=1}^{N} \sum_{j=1}^{N} U_{ij} + \frac{1}{3!} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} U_{ijk} + \cdots,$$
(3.1)

where the first term U_i is the self-energies of the atoms, the second term U_{ij} represents the two-body interactions, the third term U_{ijk} is the there-body interactions. The contribution to the energy usually decreases as the order increases. The potential models used in this thesis do not include three body or higher order terms.

In the interatomic potential method, normally, the lattice and defect energies of the ionic and semi-ionic materials are based on the Born model [100] of the solid, which describe the solid by pairwise terms with long-range interactions and short-range repulsive terms.

3.2.2 Pairwise Potentials

The long range interactions are described by the pairwise Coulomb potential which is the most important part for calculating the energy:

$$U_{ij}^{\text{Coulomb}} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}, \qquad (3.2)$$

where *q* is the charge, ε_0 is the permittivity and r_{ij} is the distance between two ions *i* and *j*. Despite the simplicity of Coulomb's law, it is complicated to sum for a periodic system. In particular the summation for an infinite periodic solid can be conditionally convergent, which is addressed by the widely used Ewald summation [101] which effects a partial transformation into reciprocal space.

The two-body short range interactions, are commonly modelled by the Buckingham potential [102], Lennard-jones potential [103] and polynomial harmonic potential.

The Buckingham potential can be represented as

$$U_{ij}^{\text{Buckingham}} = A_{ij}e^{-r_{ij}/\rho_{ij}} - \frac{C_{ij}}{r_{ij}^6}, \qquad (3.3)$$

where A_{ij} , ρ_{ij} and C_{ij} are parameters for each interaction pair.

The Lennard-Jones potential has the following form:

$$U_{ij}^{\text{Lennard-Jones}} = \frac{A_{ij}}{r_{ij}^{\text{m}}} - \frac{C_{ij}}{r_{ij}^{\text{m}}}, \qquad (3.4)$$

where A_{ij} and C_{ij} are constants.

In this thesis, we also used the polynomial potential as given by

$$E^{Polynomial} = C_0 + C_1(r - r_0) + C_2(r - r_0)^2 + \dots + C_n(r - r_0)^n, \quad (3.5)$$

where C_0 , C_1 , C_2 , C_n are constants.

3.2.3 Shell Model

To model polarisable ions, polarisation effects need to be incorporated into the Born model. The most popular and accurate way is the shell model. In this thesis, the sum charge of the core and the shell is equal to the formal charge of the ion.

In the shell model, atoms are considered as a charged core connected to a massless charged shell by an harmonic spring.

The ionic polarizability is given as

$$\alpha = \frac{Y^2}{k},\tag{3.6}$$

where Y is the charge of the massless shell, k is the harmonic spring constant, A dipole is created by the displacement of the shell relative to the core. Short range interactions are normally taken as acting through the shells.

Standard procedures are available for undertaking summations which for the Coulomb term, as noted, use the Ewald technique, while for short range terms employ real space summations up to a specified cut-off. Derivatives may also be calculated from which properties such as elastic, dielectric and lattice dynamical properties may be calculated.

3.2.4 Mott Littleton approach

In the Mott-Littleton approach [104], the defective structure is divided into two regions, with the point defect at the centre of the inner spherical region (region 1). The atoms in region 1 are assumed to be strongly perturbed by the defect. Therefore, interactions between atoms in region 1 are treated most accurately with explicit relaxation with respect to their Cartesian coordinates. Beyond region 1, Region 2 is treated using the approximation of linear response theory, in which the potential energy is assumed to be harmonic and forces linear around the equilibrium with respect to atomic coordinates and is divided into subregions 2a and 2b. This approximation allows us to determine ionic displacements in region 2 in response to a perturbation due to a defect in region 1. 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 2a and a more approximate treatment of the further region 2b extending to infinity, where only long-range Coulomb interactions with the defect are considered.

The total energy is calculated by:

$$E = E_1(x) + E_{12}(x, y) + E_2(y), \qquad (3.7)$$

where *x* is the coordinate and *y* is the displacement of the ions, E_1 is the energy of region 1, E_{12} is the interaction between region 1 and region 2, E_2 is the energy of region 2.

3.3 Quantum Mechanical Methods

Atomistic simulations based on interatomic potentials neglect the quantum aspects of the nuclear and electronic degrees of freedom, so that the electron structures or electron state cannot be calculated. Quantum Mechanics (QM) can be used to construct realistic models of electrons in many-body systems. In QM, all particles including electrons behave like waves, and the wave function is used to describe the behaviours of these waves. There are two widely used QM methods: Hartree-Fock (HF) and Density Functional Theory (DFT). The many body wave function is constructed from single particle wave functions in HF method, while in DFT, instead of the many body wave function, the charge density of the system constructed by the single particle wave function is used.

3.3.1 Schrödinger equation

Schrödinger equation is a linear partial differential equation which describes the wave function or state function of a quantum mechanical system.

The time-independent Schrödinger equation form is

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(r) = \widehat{H}\psi(r) = E\psi(r), \qquad (3.8)$$

where \hbar is a modification of Planck's constant (h/2 π), *m* is the mass of the particle, ∇^2 is the Laplacian, V(r) is the potential energy at point r, \hat{H} is the Hamiltonian operator, $\psi(r)$ is the wavefunction and *E* is the total energy. The energy of a system can be obtained by solving this equation.

The Hamiltonian operator can be further divided into electronic and nuclear operator components as:

3.3 Quantum Mechanical Methods

$$\widehat{H} = K_N + K_E + V_{NN} + V_{NE} + V_{EE} , \qquad (3.9)$$

where K is kinetic energy, V is potential, N is nuclear and E is electronic.

The Schrödinger equation can only be solved accurately in a few cases, *e.g.* the free electron. For the system with more than one electron or particle, most solutions calculated are only approximations of the exact solution. Therefore, to find the most accurate solution, precise representations of many body wave functions need to be found.

The first approximation is the Born-Oppenheimer (adiabatic) approximation. [105] This approximation is the assumption that the electronic motion and the nuclear motion can be separated, because the nuclei are much heavier and slower than the electrons. Considering the electronic degrees of freedom, with frozen nuclear positions, the nuclear kinetic energy term can be neglected, and the nuclear repulsion can be applied as a constant for a given configuration of nuclei. Based on this, the electronic part of the Schrödinger equation is separated from the nuclear part:

$$E_e \psi = \hat{H}_e \psi = (K_E + V_{NE} + V_{EE})\psi, \qquad (3.10)$$

where ψ is the many-electron wave function that depends parametrically on the positions of the nuclei, E_e is the electronic energy, \hat{H}_e is the electronic Hamiltonian which only contains the electronic part of equation 3.9.

This approximation works for most systems but cannot deal with extremely light nucleated species or systems in the excited state. For more complicated problems, such as heavier atoms, molecules, the number of particles and degrees of freedom increases. Further approximations are needed to get exact solution for many-body system in which the motions of the nuclei, the electron-electron interactions need to be considered.

3.3.2 Hartree-Fock method

The Hartree-Fock (HF) method solves the Schrödinger equation based on the single electron wave function by assume that the *N* electrons in the system are independent particles, occupying single electron spin orbitals ($\psi_N(r)$) with

single electron wave functions. The initial many body wave functions can be representing as a set of spin orbitals:

$$\psi(x_1, x_2, x_3, \dots x_N) \approx \psi_1(x_1)\psi_2(x_2)\psi_3(x_3)\dots\psi_N(x_N)$$
, (3.11)

where *N* is the number of electrons. The Hartree equations are numerically solved by the self-consistent field (SCF) methods, but this rough approximation does not satisfy the Pauli exclusion principle. The Pauli exclusion principle stipulated that no two particles of half-integer spin (fermions) can occupy the same quantum state. For a two particle system with two identical independent particles 1 and 2, for example, with wave functions ψ_i and ψ_j that describe two quantum states i and j, respectively (with i and j comprising all quantum numbers which identify the two states), the wave function of the system can be $\psi_{ii} = \psi_i(x_1)\psi_i(x_2)$. Because the two particles are identical and indistinguishable, the same system state can be achieved if particle 1 occupies state *j* and particle 2 is in state *i*, resulting in another system wave function $\psi'_{ij} = \psi_j(x_1) \psi_i(x_2)$. That is the same system is represented by two different wave functions, ψ and ψ' , producing two different sets of physical properties, which would be physically unreasonable. A choice of the system wave function as a linear combination of ψ_{ij} and ψ'_{ij} avoids this problem.

The Pauli exclusion principle requires the many body wave function is antisymmetric with respect to interchange of any two electron coordinates:

$$\psi(x_1, x_2, x_3, \dots x_N) = -\psi(x_1, x_2, x_3, \dots x_N), \qquad (3.12)$$

which implies for the two independent electrons $\psi = \psi_{ij} - \psi'_{ij}$. The minus sign here makes the wavefunction to vanish if both states are *i* or *j*, therefore both electrons cannot occupy the same state.

Instead of using the simple form of the wavefunction shown in equation 3.11, a Slater determinant [106] is used to construct a properly antisymmetric normalised wavefunction of N particles:

$$\psi(x_1, x_2, x_3, \dots x_N) = \frac{1}{\sqrt{N}} \det[\psi_1(x_1)\psi_2(x_2)\psi_3(x_3)\dots\psi_N(x_N)].$$
(3.13)

The total energy is:

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$$E = \langle \psi | \hat{H} | \psi \rangle = \sum_{i=1}^{N} H_i + \frac{1}{2} \sum_{i,j=1}^{N} (J_{ij} - K_{ij}).$$
(3.14)

The first term deals with the kinetic and potential energy due to interaction with electrons and atomic nuclei:

$$H_i = \int \psi_i^*(x) \left[-\frac{1}{2} \nabla^2 + V(x) \right] \psi_i(x) \, dx \,. \tag{3.15}$$

The second term deals with the electron-electron interactions, where J_{ij} is the Coulomb integral:

$$J_{ij} = \iint \psi_i^*(x_1)\psi_j^*(x_2)\frac{1}{r_{12}}\psi_i(x_1)\psi_j(x_2)\,dx_1dx_2\,,\qquad(3.16)$$

and K_{ij} is the Exchange integral:

$$K_{ij} = \iint \psi_i^*(x_1)\psi_j^*(x_2)\frac{1}{r_{12}}\psi_i(x_2)\psi_j(x_1)\,dx_1dx_2\,. \tag{3.17}$$

The HF method has been widely used and can give useful results for total energies and estimates of bonding and geometry. But the HF fails accurately to describe electron correlation. By including the electron correlation energy or approximations to the energy, the post Hartree-Fock method allows accurate descriptions of electronic system. However, these methods are very computationally expensive.

As noted, the HF method is based on a many electron wavefunction. Density Functional Theory (DFT), discussed in the next section, replaces the multi-body electron wavefunction with the electron density, which helps to make calculations with an acceptable level of accuracy on large systems more tractable.

3.3.3 Density Functional Theory

Density functional theory (DFT) is a computational quantum mechanical modelling technique that can predict the electronic structure in a multi-electron system of many-body systems, in particular atoms, molecules, and condensed phases. The DFT method has become a very widely used method for calculating the electronic structure of the ground state of matter with its extensive accuracy, applicability and computational economy.

Density functional theory was developed in the 1960s on the basis of the Thomas-Fermi model [107, 108], which describes the physical properties of the ground state of a system by means of particle densities.

The electronic kinetic energy obtained by integrating the kinetic energy density of a homogeneous electron gas as:

$$T = \frac{3}{10} [3\pi^2]^{2/3} \int n(r)^{5/3} dr = C_k \int n(r)^{5/3} dr.$$
(3.18)

The potential energy due to the attraction between the nuclei and the electrons is:

$$V_{eN} = \int n(r) V_N(r) dr \,. \tag{3.19}$$

The potential energy due to the electron-electron interactions of the system, which is approximated by the classical Coulomb repulsion between electrons is:

$$V_{ee} = \frac{1}{2} \iint \frac{n(r)n'(r)}{|r-r'|} dr dr' .$$
(3.20)

The Thomas-Fermi energy is composed of the kinetic and potential energies:

$$E^{TF}[n(r)] = C_k \int n(r)^{5/3} dr + \int n(r) V_N(r) dr + \frac{1}{2} \iint \frac{n(r)n'(r)}{|r-r'|} dr dr'. \quad (3.21)$$

Although DFT originated in Thomas-Fermi theory, DFT did not have a firm theoretical basis until Hohenberg-Kohn theorem [109] was proposed. The first theorem of Hohenberg-Kohn states that the ground state energy of the full fermion subsystem without spin is a unique function of the particle density function, that is, the physical properties of the ground state of the system are determined by the population density function. The second Hohenberg-Kohn theorem proves that, under the condition of a constant number of particles, the ground state energy equals the total energy functional and takes the minimum value of the correct particle number density function. That is to say, under the condition of constant number of particles, the energy functional to the density functional variation gives the energy of the ground state of the system. The energy functional can be written as:

3.3 Quantum Mechanical Methods

$$E^{HK}[n(r)] = \int n(r)V(r)dr + F[n(r)], \qquad (3.22)$$

Where the F[n(r)] functional is unknown and all properties of the system are calculated from the electron density *V*. To solve the unspecified particle density function and kinetic energy function problem in the Hohenberg-Kohn theorem, Kohn and Sham [110] produced the famous Kohn-Sham equation. In the framework of the Kohn-Sham DFT, the complex multi-body problem (due to the interaction of electrons in an external electrostatic potential) is simplified as a problem that no interacting electrons move in the effective potential. This effective potential includes external potential fields and the effects of Coulomb interactions between electrons, such as exchange and correlation. In Kohn-Sham theory, the F[n(r)] is composed of three terms,

$$F[n(r)] = T_s[n(r)] + V_{ee}[n(r)] + E_{xc}[n(r)], \qquad (3.23)$$

where the first term $T_s[n(r)]$ is the kinetic energy of a non-interacting electron gas of density n(r), the second term $V_{ee}[n(r)]$ is the classical electrostatic energy of the electrons as equation (3.20) and the third term $E_{xc}[n(r)]$ is the exchange-correlation energy which contains the difference between the exact and non-interacting kinetic energies and also the non-classical contribution to the electron-electron interactions. The first two terms are known exactly and contribute the majority of the energy, the third being a small unknown quantity.

The total energy of the system is expressed as

$$E^{KS}[n(r)] = \int n(r)V(r)dr + T_s[n(r)] + V_{ee}[n(r)] + E_{xc}[n(r)]. \quad (3.24)$$

3.3.4 Pseudopotentials

To make the problem of describing very many particles tractable in quantum chemistry two further approximations are widely used. First, the one electron wave functions, i.e. orbitals are represented by linear combinations of basis functions. In our work, we employ the GAMESS-UK package where basis functions are chosen as atomically centred Gaussian functions [111, 112]:

$$\chi(\zeta, n, m, l; r, \theta, \phi) = NY_{l,m}(\theta, \phi)r^{2n-2-l}e^{-\zeta r^2}, \qquad (3.25)$$

3.3 Quantum Mechanical Methods

where *N* is a normalization constant, ζ is the exponent, $Y_{l,m}$ are spherical harmonic functions, *n*, *m*, and *l* indices determine the type of orbital (*s*, *p*, *d*,etc.).Details of the basis used will be given below in the next section. Second, to save the calculation costs, the pseudopotential (also called Effective Core Potential, ECP) approximation treats the core electrons and the valence electrons separately. The explicit description of the core electrons of an atom is replaced with an effective potential, or pseudopotential. Usually, the potential matches the core potential exactly outside a chosen core radius, but varies smoothly within the core radius, to avoid the large oscillations of the wave function in this region.

To describe a point defect in an extended system such as a 3-dimensional periodic solid, e.g. a TCO semiconductor, in this work, we will use an embedded cluster approach. [113] Therein a region of interest around a point defect is treated with a QM method of choice, whereas the effect of the system remainder is represented by an embedding potential in the QM Hamiltonian. Such an embedding potential will include long-range Coulomb contributions and short-range terms due to Pauli repulsion and localisation of the explicitly treated electrons in the QM region. The latter contributions are especially important to include for cations surrounding the QM region as negatively charged electrons would naturally be attracted to positive centres of the environment. Conventionally, these interactions are represented by pseudopotentials – compared to ECP electrons of the environment rather than of the core are now replaced by the potential. It is convenient to choose embedding pseudopotentials in the same form as that of the ECP as it allows to use common QM packages such as GAMESS-UK without or with a minimum of modifications. In this thesis, a specially designed local ECP was used for this purpose as detailed in the next section.

3.3.5 QM/MM techniques

The QM/MM model uses a system of five approximately concentric regions. Regions 1-3 are part of the active region which will undergo geometry optimization, Regions 4 and 5 are frozen and no changes can be made to any of the species within them. Region 1 contains the central defect and its surrounding atoms, typically of the order of 100 atoms (97 for In_2O_3 , 86 for ZnO in this thesis), is treated with a QM method.

In this thesis, we use DFT with a tripple zeta plus polarization Gaussian basis set for oxygens (Def2-TZVPP) [114] and a double zeta plus polarization set for In and Zn cations (cc-pVDZ-PP). [115, 116] To reduce the computational load, we have removed *f* functions from the oxygen basis set and some of the highly diffuse functions from the cation basis sets, which do not contribute to the bonding in thesis ionic solids. The resulting reduced basis set was carefully optimised to reproduce the total energy and eigenstates of the appropriate isolated ions.

For electron exchange and correlation, we have employed three hybrid functionals, BB1k functional [117], which has been fitted to both thermochemical and kinetic data including 42% exact exchange; the PBE0 functional [118], which is frequently used in plane-wave basis calculations including 25% exact exchange; and the B97-2 functional [119], which has been fitted to a broad range of thermochemical date with 21% exact exchange.

In order to embed the QM cluster within a polar environment, Region 3 and 4 (9704 for In_2O_3 , 10460 for ZnO in this thesis) is treated with the MM method using interatomic force fields. [120] Details on forcefields can be found in Ref. [25] for In_2O_3 and Ref. [120] for ZnO.

Between the QM and MM region, a 5Å thick interface region is introduced as Region 2. Here, semi-local atom-centred pseudopotentials (similar to effective core potentials, or ECPs commonly used in quantum chemical calculations of heavy atoms) are placed on cationic sites that describe the short-range embedding potential acting on the electrons in the QM region and that prevent spillage of electronic density from the QM to the MM regions. In this thesis, a 10 electron ECP for Zn [116] and 29 electron ECPs for In [121] were used. The pseudopotential used in this study has the form:

$$r^{2}U_{p}(r) = A_{1}r \exp(-Z_{1}r^{2}) + A_{2}r^{2}\exp(-Z_{2}r^{2}) + A_{3}r^{2}\exp(-Z_{3}r^{2}), \quad (3.26)$$

where the parameters A_i and Z_i are fitted in order to minimize the gradients on the ions in the QM and interface region and the spread of deep core levels in the energy spectrum. The specially designed local ECP parameters for In and Zn are taken from Buckeridge *et al.* [42], as given in Table 3.1.

	i	A _i	Z_i
In	1	-41.9141	30.1562
	2	16.3490	1.5145
	3	0.3166	0.3335
Zn	1	-11.3067	22.6000
	2	39.4802	4.9852
	3	0.0579	0.1781

Table 3.1 Embedding cation ECP parameter in atomic units in ZnO. [42]

The long-range embedding potential is provided by the point charges on the MM centres surrounding the QM region. The effect of the whole QM/MM model termination is cancelled by the use of a group of compensating point charges that are placed around the cluster to reproduce the Madelung potential and field at lattice sites in the central active part of the QM/MM model. To account for the missing polarisation effects outside the active region, an *posteriori* correction to the total energy of a charged defect is introduced using Jost's formula:

$$E_{pol} = -\frac{Q^2}{2R} \left(1 - \frac{1}{\varepsilon^0} \right), \qquad (3.27)$$

where *Q* is the charge on the defect, *R* is the radius of the active region and ϵ^0 is the permittivity. For vertical processes of charge state change from *Q* to *Q*+ ΔQ with only electronic relaxation, we us Jost's correction:

$$E_{vertical \, pol} = -\frac{(Q + \Delta Q)^2}{2R} \left(1 - \frac{1}{\varepsilon^{\infty}}\right) + \frac{Q^2}{2R} \left(\frac{1}{\varepsilon^{\infty}} - \frac{1}{\varepsilon^0}\right),\tag{3.28}$$

where $E_{vertical pol}$ is the vertical polarization energy, and ε^{∞} is the highfrequency permittivity. The hybrid QM/MM embedded cluster approach used is implemented in the CHEMSHELL [122] package. The QM/MM energy is obtained in an additive approach as a sum of QM and MM terms with the interaction energy between the two regions accounted for by the QM term whose Hamiltonian includes the embedding potential. The GAMESS-UK [123] code is employed in QM calculations, while the GULP package has been used to calculate MM contributions.

The advantages of this method are a comprehensive account of short and longrange polarization effects of a charged defect; the lack of periodic image interactions; and access to the vacuum level, which allows ionization energies to be determined with an absolute reference.

3.4 Point Defects in Semiconductors

3.4.1 Compact and diffuse defect states

A defect can have several competing electronic states, including the compact state and the diffuse state. The ground state of the defect will be the lower energy state, but under non-equilibrium conditions (such as the optical ionisation transitions), transitions between states can occur. Previous studies have focused on the compact nature of the defect, where the carriers are completely bound to the defect and individual atoms around it, and only the ionization to or from the energy band is considered. However, in dielectrics, a point defect can trap one or more charged carriers (depending on the charge amount of the defect) to form a shallow, diffuse hydrogenic orbitals, especially when the potential for forming such a diffuse state is an attractive Coulombic well. The energy level of the diffuse *s*-like carrier will shift into the gap relative to the band edge (depending on the defect charge state), and the ground state of the corresponding defect can be either its diffuse state, or the corresponding compact state. The holes in the compact state are completely bound to the defect and have a very local wave function. The wave function of the diffuse state has a larger distribution range, which diffuses in the defect and several atoms around the defect, as shown in Figure 3.1. These two states can coexist, and transitions can happen between them, which may be observable depending on both the property of the defect and the kinetics of the experiment.

The diffuse state energy level can be calculated from the effective mass theory. [124]



Figure 3.1 A schematical comparison between a compact state and a diffuse state. The blue lines represent the wave function ψ , the black line represents the shape of the electrostatic potential.

In effective mass theory, the bands for the semiconductor are assumed as isotropic, nondegenerate, and parabolic. The energy (in atomic units) of hydrogenic defect traps for electrons and holes is

$$E_H = -\frac{Z^2 m^*}{2\varepsilon^2}, \qquad (3.29)$$

where Z is the charge state of nuclei (compact state), m^* is the electron/hole effective mass, ε is the static dielectric constant.

The energy of helium defect traps for two electrons or two holes is

$$E_{He} = \frac{m^*}{\epsilon^2} (I_1(He) + I_2(He)), \qquad (3.30)$$

where $I_1(He)$ is the first ionisation energy and $I_2(He)$ is the second ionisation energy of helium.

The energy of hydride defect traps for two electrons is

$$E_{Hydride} = \frac{m^*}{\epsilon^2} (I_1(H) + A(H)), \qquad (3.31)$$

where $I_1(H)$ is the first ionisation energy of hydrogen and A(H) is the electron affinity of hydrogen.

3.4.2 Formation energies

The formation energy of a defect *X* in charge state q ($E_f[X^q]$) is determined as [125]:

3.4 Point Defects in Semiconductors

$$E_f[X^q] = E[X^q] - E_0 - \sum_i n_i \mu_i + q E_F , \qquad (3.32)$$

where $E[X^q]$ is the total energy of the defective structure, E_0 is the energy of the perfect crystal, n_i is the number of atoms of species i (host atoms or impurity atoms) that have been added to $(n_i > 0)$ or subtracted from $(n_i < 0)$ in forming X, μ_i is the chemical potential of species i, and E_F is the Fermi energy.

A diagram (Figure 1 in Ref [126]) is used to illustrate the formation energy as a function of the Fermi-level position and for various charge states q as shown in Figure 3.2. For a neutral defect, q = 0; if one electron is removed, q = +1; if one electron is added, q = -1. In the semiconductor, the defect can exhibit various charge states. In the diagram, The zero point of the abscissa is the valence band maximum (VBM), the dotted line is the conduction band minimum (CBM). The solid black lines are the formation energy defined by Equation (3.33), and the slope of the lines indicate different charge states, the point of intersection of the solid black lines indicate the transition levels (deep donor level ε (+/0) and deep acceptor level ε (0/-)). The solid red lines indicate the energetically most favourable charge states for a given Fermi level.



Figure 3.2 Formation energy diagram.

3.4.3 Ionization energies as defect (transition) levels

Understanding vertical ionization potentials and electron affinities can provide information on many defect processes that play a key role in light absorption and luminescence, and charge trapping. A conventional configurational coordinate diagram [127] (Figure 4.10 in Ref [128]) is used to analyse the optical properties of the defects.

As shown in the lower part (blue) of Figure 3.3, an electron trapped by an acceptor in the ground state (A^{-}) can be excited to the conduction band if it absorbs a photon with sufficient energy (E_{ab}) , the resulting configuration being the neutral charge state plus a conduction electron, $A^0 + e^-$. The defect in the ionised state will relax (E_{rel}*) before emitting a photon and returning to its ground state via an electron-hole recombination. The relaxation lowers the energy of the ionised state as the surrounding atoms move to new stable positions. On emission, a conduction band electron undergoes a vertical transition from the conduction band to the empty defect state (A^0) , i.e. recombining with the hole bound to the acceptor, giving rise to a PL (E_{PL}). Again, the atoms around the defect relax back to the initial ground state (E_{rel}) after the optical emission. An analogous process will involve a hole ionisation from an acceptor, which, in other words, describes a capture by the acceptor of an electron from the valence band—see the upper part of the configurationcoordinate diagram shown in Figure 3.3. The energy difference between the minima of the ionised and ground states can be identified in the PL spectra as a zero-phonon line (ZPL). [128]

3.4 Point Defects in Semiconductors



Figure 3.3 A configuration-coordinate (q) diagram of ionisation and capture by an acceptor A of an electron, e^- shown in blue—A(-1|0)e—and of a hole, h⁺ shown in red—A(0|-1)h. [128]

3.4.4 Charge carrier and defect concentrations

The concentration of each defect X in each charge state q is given by:

$$C_{X^q} = N_X g_{X^q} exp\left(-\frac{E_f(X^q)}{kT}\right),$$
(3.33)

where N_x is the density of sites in which the defect may form, g_x^q is the degeneracy of the charge state, E_F is the self-consistent Fermi energy, k is Boltzmann's constant.

The electron (n_0) and hole (p_0) carrier concentrations can be determined by integrating the density of states weighted by the appropriate Fermi-Dirac function:

$$n_0 = \int_{E_g}^{\infty} f_e(E)\rho(E)dE , \qquad (3.34)$$

$$p_0 = \int_{-\infty}^0 f_{\rm h}(E)\rho(E)dE , \qquad (3.35)$$

where $f_e(E) = [\exp((E_F - E)/kT) + 1]^{-1}$ is the Fermi-Dirac distribution function and $f_h(E) = 1 - f_e(E)$.

The self-consistent Fermi energy and equilibrium defect and carrier concentrations are determined from the computed formation energies using a Fortran code 'SC-FERMI". [129]

3.5 Computational Codes

3.5.1 General Utility Lattice Program (GULP)

The General Utility Lattice Program (GULP) [130, 131] can perform a wide range of simulations of solids surfaces, defects and, clusters using interatomic potential methods. GULP can be used to perform geometry optimizations and Mott-Littleton calculations and can find transition states for ionic migration processes using the "Nudged Elastic Band" approach.

In this work, the interatomic potential calculations of defect formations and energies of both In_2O_3 and SnO_2 (see Chapter 4) are performed using MM Mott-Littleton procedure as implemented in GULP.

3.5.2 ChemShell

ChemShell is a computational Chemistry environment which support hybrid quantum mechanical/molecular mechanical (QM/MM) calculations. [122, 132] It has interfaces with a range of other Quantum Mechanical and Molecular Mechanical codes including GAMESS-UK [123] and GULP.

We carried out a more sophisticated and accurate QM/MM calculations to simulate the defect properties of In₂O₃ and ZnO (see Chapter 5-8) using the Embedded Cluster Technique employing ChemShell.

3.5.3 Knowledge Led Master Code (KLMC)

Our in-house code Knowledge Led Master Code (KLMC) [133] automates many repetitive or complex tasks, traditionally performed by the user, using a range of third party codes. The applications of KLMC include simple task farming; structure prediction of nanosized clusters, surfaces, and bulk phases using a range of global optimization techniques based on basin hopping and genetic algorithms; exploration of ergodic regions and statistical sampling of solid solutions or multiple point defects in a crystalline solid.

In this Thesis, random structure generations and global minimum simulations for the solid solutions of In_2O_3 and SnO_2 simulations are carried out using

KLMC in conjunction with third party coded GULP and Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). [134]

3.5.4 SC-FERMI

SC-FERMI [129] is a Fortran code that calculates the self-consistent Fermi level and defect concentrations given a set of formation energies (at VBM). The inputs include the defect formation energies, density of sites where they can form, and the degeneracy of each charge state; the material bandgap; and the calculated density of states of the pristine system. The output is the self-consistent Fermi energy E_F , the total concentrations of each defect as well as the concentration of its individual charge states, and the free carrier concentrations.

3.6 High Performance Computing (HPC)

The calculations of this Thesis have been run on several HPC systems, including two UCL-based and two national HPC.

The QM/MM calculation of defects In₂O₃ and ZnO (Chapter 5-8) was performed on Archer. Archer is the UK National Supercomputing Service, provided for two research Councils (EPSRC, NERC,) and managed by Edinburgh Parallel Computer Centre (EPCC), using technology supplied by Cray Inc. It is designed for calculations that require large numbers of cores working in parallel.

The solid solutions of In₂O₃ and SnO₂ simulations (Chapter 9) are carried out on UCL-based Legion, Grace and UK National Tier 2 HPC Thomas.

Time to run calculations on Archer and Thomas was requested and granted through my membership of the UK's HEC Materials Chemistry Consortium, which is funded by EPSRC (EP/L000202, EP/R029431). This work made use of computational support by CoSeC, the Computational Science Centre for Research Communities, which was made available through my membership of the EPSRC funded Materials Chemistry High End Computing Consortium (MCC).

Interatomic Potentials and Defect Structures of In₂O₃ and SnO₂

4.1 Introduction

In this Chapter, we will focus on the defect structure of In_2O_3 and SnO_2 materials and of the relationship between their defect and electronic properties. In In_2O_3 and SnO_2 , as discussed in Chapter 2, the *n*-type conductivity has intuitively been attributed to the presence of oxygen vacancies, but other sources have also been proposed [14-17] and the matter remains a topic of debate. Accurate modelling of intrinsic and extrinsic defects is needed to understand the source of the conductivity.

ITO (indium tin oxide) is a disordered system, which necessitates large length scale simulations of multiple atomic environments in the presence of charge carriers to understand its structural 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 In₂O₃ and SnO₂ compounds. In this Chapter, we demonstrate the first transferable interatomic potential model, that reproduces well both the structure and physical properties of In₂O₃ and SnO₂

including their dielectric response and lattice energies. We then apply our models to develop a consistent and reliable set of models for the defect structure of the materials.

For TCO materials, native defects may act as donors resulting in intrinsic ntype conductivity as has been recently demonstrated by Buckeridge et al. [42] Further extrinsic doping such as Sn in In₂O₃ is, however, required to achieve technologically desired concentrations of charge carriers. Hence, the main aim of this Chapter is to explore defect properties of both SnO₂ and In₂O₃ 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 reproduces the physical 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 In₂O₃ and SnO₂. 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. help explain experimental observations The results regarding the configurations of tin clusters in ITO.

4.2 Approach and settings

The lattice and defect energies in this Chapter are based on the Born model of the ionic solid [20], discussed in the previous Chapter 3.2.2. The pairwise interactions between the ions are modelled by a combination of the Buckingham [135], Lennard-Jones, constant offset and polynomial harmonic potentials to describe a smooth monotonically decaying functions as shown in Figure 4.1. The 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 SnO₂ and In₂O₃.

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 SnO₂ and penalise a hypothetical anatase phase of this material. One possible rationalisation is that the unusual trigonal structure 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 SnO₂.

Careful choice of the potential parameters is crucial for accurate modelling of both structural and physical properties, which we will address in section 4.3 below. The parameters of our model, obtained by empirical fitting as discussed below are given in Table 4.1.

The resulting potentials were used to study point defects in both In_2O_3 and SnO_2 , using the Mott-Littleton method [136, 137] as implemented in GULP.

In this work, the radius of region 1 is chosen as 15 Å (so that there are 1093 atoms for In_2O_3 and 1189 for SnO₂ in the region) with a 30 Å radius for region 2a, 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 to or 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 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.

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Figure 4.1 Interatomic potential model for In_2O_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 others previously published (see text for details).

The first interatomic potentials for SnO₂ reported by Freeman *et al.* [37], were fitted to static and high frequency dielectric and elastic constants of SnO₂; the lattice energy and lattice parameter though were less well described, as shown in Table 4.3. A parameterisation of the Buckingham potential for In₂O₃ based on the oxide parameters of Freeman *et al.* [37] and Bush *et al.* [135], with In-O parameters of McCoy *et al.* [138] was reported by Warschkow *et al.* [22], in which the dielectric properties were not, however, fitted. Walsh *et al.* [25] reported an alternative parameterisation, which in contrast reproduced well the static and high-frequency dielectric constants (see Table 4.4), but the lattice energy again deviated from experiment and the oxide parameters were incompatible with Freeman's SnO₂ 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 In₂O₃ and SnO₂ (as summarised in Table 4.1). The present interatomic force field is a revised potential which reproduces better the structure and dielectric constants compared to the set of interaction parameters summarised as P-1 in Table 4.2. The new model was obtained by empirical fitting, using the GULP code, to calculated lattice parameters, lattice energy, static and high-frequency dielectric constants and gave a better agreement with the experimental data compared to earlier work, as shown in Table 4.3 and Table 4.4.

(a) Buckingham potential								
Interaction	A (eV)	ρ (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	41944.48	0.20	0.00					
(b) Lennard-Jones p	ootential							
Interaction	A (eV Å ^m)	<i>B</i> (eV Å ⁿ)	т	n				
Sn core - Sn shell*	0	2.00	12	6				
Sn shell – Sn shell	1	0	18	1				
Sn shell - O 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	1	0	18	1				
In shell – O shell	1	0	18	1				
O core - O shell	10	0	12	6				
(c) Polynomial poter	ntial							
Interaction	n	C_0	r _{min}	r _{max}				
Sn shell - O shell	1	-1.567	0.00	2.15				
In shell - O shell	1	-0.65	0.00	2.30				
(d) Polynomial harm	nonic potential							
Interaction	n	C_0	C ₁	C ₂	r min	r _{max}		
Sn shell - O shell	2	-280.31	236.42	-43.67	2.15	2.30		
In shell - O shell	2	-44.17	47.29	-11.41	2.30	2.70		
(e) Shell model								
Species	Y (e)	<i>k</i> (eV Å ⁻²)						
Sn	4.34	94.05						
In	2.63	7.53						
0	-3.16	70.51						

Table 4.1 Interatomic Potential Parameters for SnO_2 and In_2O_3 .

*The interaction between one atom's core and another atom's shell.

(a) Buckingham potential								
Interaction	A (eV)	ρ (Å)	C (eV Å ⁶)	Cutoff				
Sn shell - O shell	1588.75	0.33	0.00	15				
Sn shell - Sn shell	0.10	0.30	2.00	15				
In shell - O shell	1914.95	0.32	30.00	15				
In shell - In shell	0.00	0.30	28.00	15				
O shell - O shell	24.66	0.50	32.61	15				
O core - O shell	41944.48	0.20	0.00	15				
(b) Lennard-jones potentials								
Interaction	A (eV Å ^m)	<i>B</i> (eV Å ⁿ)	т	n				
O core - O shell	10	0	12	6				
Sn core - Sn shell	0	0	12	6				
(c) Shell model								
Species	Y(e)	K (eV Å-2)						
Sn	4.34	94.05						
In	2.63	7.53						
0	-3.16	70.51						

$Table 4.2$ Interatorne r dentiar ranameters for SHO_2 and H_2O_3 (r - 1).	Table 4.2 Ir	nteratomic	Potential	Parameters	for	SnO ₂	and In	20_{3}	(P-1)	
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Note. Short-range interaction cut-offs are set to 15 Å.

Parameter	Experimental	P1	Present	Freeman et al.
			work	[37]
Lattice parameter, a(Å)	4.737	4.737	4.742	4.706
	[139],4.738			
	[140]			
Static dielectric constant	14.0 [141]	16.761	16.724	13.8
High frequency dielectric	3.785 [141]	3.914	3.889	3.894
constant				
Lattice energy (eV)	-122.125	-113.72	-122.32	-110.68
Elastic constants [142]				
C ₁₁ (GPa)	261.7	310.42	290.55	299
C ₁₂ (GPa)	177.2	201.65	191.07	212
C ₁₃ (GPa)	156.0		249.45	198
C ₃₃ (GPa)	450.0		620.61	522
C ₄₄ (GPa)	103.07	113.98	119.20	111
C ₆₆ (GPa)	207		236.36	228

Table 4.3 Calculated and experimental crystal properties of SnO₂.

Table 4.4 Calculated and experimental crystal properties of In_2O_3 .

Parameter	Experimental	P1	Present	Walsh et	Warschkow et	Mccoy et
			work	<i>al.</i> [25]	al. [22]	<i>al.</i> [138]
Lattice parameter,	10.117 [143]	10.121	10.119	10.121	10.120	10.115
a(Å)						
Static dielectric	8.9-9.5 [144]	9.136	9.191	9.052	6.872	9.455
constant						
High frequency	4 [145]	3.937	3.941	3.903	3.534	4.907
dielectric constant						
Lattice energy (eV)	-149.98	-	-150.01	-140.60	-141.91	-141.14
		142.34				
Elastic constants						
C11 (GPa)		346.30	337.14	297.75	368.10	324.4
C ₁₂ (GPa)		155.48	154.99	141.78	150.11	151.7
C44 (GPa)		94.08	93.19	76.42	111.24	120.7

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

4.4 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 hypothesizing that the valence band maximum can be represented by an hole localised on an anion, the conduction band minimum by an electron on a cation, and take the difference in energy between the two. Such an assumption is broadly supported by ab initio calculations on ionic compounds of normal metals, including both SnO₂ and In₂O₃. In our model, the hole state is obtained by instantaneous ionisation of an oxide ion including highfrequency 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 Waddington [146], cf. 8.75 eV from ref. Freeman et al. [37], 8.89-9.58 eV from Ladd and Lee et al. [147]). For the electron, the localised state would be the Sn^{3+} (for SnO_2) or In^{2+} (for In_2O_3) ion on the appropriate cation site (Sn_{Sn}' or In_{In}' in 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 required quantities are collected in Table 4.5 for SnO₂ and Table 4.6 for In₂O₃.

The calculated band gap of SnO₂, by this crude procedure, is 5.21 eV, compared with the experimental value of 3.6 eV. [148] For In_2O_3 , we calculate the band gap of 6.71 eV, as compared to the experimental value of 2.7 eV. [18] (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 ~0.5 eV of available experimental data [149-151]), 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 gap as a measure of electron localisation,

4.4 Electron and Hole Formation

which can subsequently be employed as a parameter of the electronic structure in calculations on more complex mixed materials including lightly-doped ITO and solid solutions between tin and indium oxides. Therefore, the corresponding corrections for the energies of the bottom of the conduction band for end member compounds are +1.65 eV and +4.01 eV of SnO₂ and In₂O₃, respectively. The large differences can be probably attributed to the more stable environment for the localised electron used to model the CBM when situated on a Sn⁴⁺ site in SnO₂ compared with an In³⁺ site in In₂O₃, due to the higher net positive charge and the shorter cation-anion bond length (circa 2.05 Å in SnO₂ vs 2.18 Å in In₂O₃).

Table 4.5 Electron-hole formation in SnO₂. The Sn_{Sn}' and O₀^{\cdot} defect energies, fourth ionisation energy of Sn and second electron affinity of O are used to compute the ionisation potential I and electron affinity A of the material, the difference of which gives the band gap.

Terms	P1(eV)	Energy (eV)	Hines	et	al.	Experimental
			[38]			band gap [148]
Sn _{Sn} ' (=e')	37.25	37.33				
O ₀ [•] (=h [•])	17.57	18.06				
O^- + e' $\rightarrow O^{2-}$	8.75	9.41				
$I = -E_h$	8.82	8.65	8.0			
$Sn^{3+} \rightarrow e' + Sn^{4+}$	40.73	40.73				
$A = -E_e$	3.48	3.40	2.5			
Band gap (correction)	5.34 (-1.74)	5.25 (-1.65)	5.5			3.6

Table 4.6 Electron-hole formation in In_2O_3 . The In_{ln} and O_0 defect energies, third ionisation energy of In and second electron affinity of O are used to compute the ionisation potential I and electron affinity A of the material, the difference of which gives the band gap.

Terms	P1(eV)	Energy (eV)	Experimental
			band gap [18]
In _{in} ' (=e')	27.08	27.10	
Oo' (=h')	16.99	17.05	
$O^- + e' \rightarrow O^{2-}$	8.75	9.41	
$I = -E_h$	8.24	7.64	
In²+ →e'+ In³+	28.03	28.03	
$A = -E_e$	0.95	0.93	
Band gap (correction)	7.39 (-4.69)	6.71 (-4.01)	2.7

Next, we turn our attention to atomic defects.
4.5 Defect energies from Mott-Littleton Calculations

The calculated intrinsic defect energies in SnO₂ and In₂O₃ are presented in Tables 4.7 and 4.8.

The rutile structure of SnO₂ has only one octahedrally coordinated lattice site for cations and one trigonal site for anions. We confirm the prediction by Hines *et al.* [38] that the interstitial crystallographic site 4c, which is in the centre of an unoccupied oxygen octahedron, has a lower energy for an oxide ion compared to the 4g site explored by Freeman *et al.* [37], 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 In_2O_3 , there are two symmetry-unique cation 6-coordinated lattice sites (the b site, which is a slightly trigonally compressed octahedral coordinated site, and the d site, which is a highly distorted octahedral coordinated site; there are three times as many d sites as there are 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 4.8, 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 A for site d). Compared to previous calculations, we predict a substantially lower energy for the oxygen at an interstitial site in In_2O_3 by ~ 5.0 eV compared to Warschkow and by ~ 1.2 eV compared to Walsh *et al.* This big difference, especially when compared to the former report, can perhaps be attributed to an incomplete relaxation (in this earlier work) 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 SnO_2 and In_2O_3 , respectively, based on an earlier more accurate simulation using a hybrid

4.5 Defect energies from Mott-Littleton Calculations

quantum mechanical/molecular mechanical (QM/MM) approach reported by Buckeridge *et al.* [42] (Note, 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 SnO₂ [37], and 20.99 eV for In₂O₃ [25].

			0	
Defect	D	efect energy (eV)		Wyckoff's site
	P1	Present work	Freeman [37]	_
Oi"	-7.64	-11.35	-8.31	4 <i>g</i>
Oi''		-11.62		4 <i>c</i>
Sni ^{·····}	-72.91	-77.08		4 <i>g</i>
Sni ^{·····}		-79.52	-68.23	4c
Vo	19.66	24.02	19.39	4 <i>f</i>
Vsn''''	89.58	98.04	87.48	2a

Table 4.7 Intrinsic defect energies in SnO₂.

Table 4.8 Intrinsic defect energies in In₂O₃.

Defect		Defect energy	Defect energy (eV)		
	P1	Present work	Walsh <i>et al.</i> [25]	site	
V ₀	20.57	23.16	20.99	48e	
V _{In} '''	51.85	55.67	49.92	8b	
VIn'''	52.37	56.16	50.05	24 <i>d</i>	
O _i ''	-11.53	-15.33	-13.29	8 <i>a</i>	
O _i ''	-13.32	-15.82	-14.61	16 <i>c</i>	
O _i ''	-9.60	-12.86	-12.08	24 <i>d</i>	
In _i	-37.01	-40.52	-35.57	8 <i>a</i>	
In _i …	-37.85	-41.68	-36.21	16 <i>c</i>	
Ini	-36.18	-39.78	-34.89	24 <i>d</i>	

4.6 Oxygen Vacancy Formation

The loss of oxygen from the lattice can be represented in Kröger–Vink notation [152] as

$$0_0^{\times} \to V_0^{\circ} + \frac{1}{2} O_{2(g)} + 2e'$$
 (4.1)

Here the reaction is assumed to occur in an environment containing an excess of $O_{2(g)}$, which is often referred to "O-rich conditions" but approximately corresponds to the sample of interest being in air at 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 given by:

$$E = E[V_0^{"}] - A_0^{1-2} - \frac{1}{2}D_{0_2} + 2E_e, \qquad (4.2)$$

where $E[V_0^{\circ}]$ is the oxygen vacancy defect energy, D_{0_2} is the oxygen molecule dissociation energy (5.136 eV [49]), A_0^{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 in strongly reducing conditions ("O-poor conditions"), oxygen vacancy creation in SnO₂ proceeds as:

$$0_0^{\times} + \frac{1}{2} \operatorname{Sn}_{(s)} \to V_0^{\cdot \cdot} + \frac{1}{2} \operatorname{Sn}_{2(s)} + 2e',$$
 (4.3)

while the defect formation energy can be written as

$$E = E[V_0^{"}] + \frac{1}{2}\Delta H^0(\text{SnO}_2) - \frac{1}{2}D_{\text{O}_2} + 2E_e - A_0^{1-2}, \qquad (4.4)$$

where $\Delta H^0(SnO_2)$ is the standard enthalpy of formation of SnO₂.

The calculated oxygen vacancy formation energy of SnO₂ is 3.40 eV under O-rich/Sn-poor condition and 0.36 eV under O-poor/Sn-rich condition. Freeman *et al.* [37] 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,

4.6 Oxygen Vacancy Formation

significantly lower than the current result. Using periodic ab initio models with the PBE0 exchange and correlation density functional, Scanlon et al. [43] have reported the corresponding doubly charged oxygen vacancy formation energy to be ca. 6 eV under O-rich, and ca. 3.4 eV under O-poor conditions (extracted from Figure 2 of ref. [43]), which is somewhat different from the result of Agoston *et al.* [153], who using the same density functional have reported the value of about 2.9 eV under O-poor conditions. More recently, Buckeridge et al. [42] 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 for the doubly charged oxygen vacancy. 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, although again an improvement on the older work; and given the uncertainty in several key terms it may be difficult to get significantly better agreement.

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 SnO₂ at atmospheric conditions, which should be comparable to O-rich conditions, is 4 eV [154]. 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 the Mott-Littleton approach. We note that the density functional theory studies mentioned above do produce results that compare well with the experimental value.

For In₂O₃, the formation of the oxygen vacancy under In-rich/O-poor condition can be described as:

$$0_0^{\times} + \frac{2}{3} \ln_{(s)} \to V_0^{"} + \frac{1}{3} \ln_2 0_{3(s)} + 2e',$$
 (4.5)

4.7 Frenkel and Schottky Defects

and the oxygen vacancy formation energy:

$$E = E[V_0^{"}] + \frac{1}{3}\Delta H^0(\ln_2 O_3) - \frac{1}{2}D_{O_2} + 2E_e - A_0^{1-2}.$$
(4.6)

We obtain the energies of 2.76 eV under O-rich/In-poor condition and -0.49 eV under O-poor/In-rich condition for In₂O₃. Compared with SnO₂, the results are in similar correspondence with embedded-cluster based calculations by Buckeridge *et al.* (2.45 eV under O-rich and -0.75 eV under O-poor using BB1k). [42] Ágoston *et al.* [153] has 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 calculation 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 that show improved agreement 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.

4.7 Frenkel and Schottky Defects

Based on the calculated point defect formation energy (Tables 4.5 and 4.6) and the calculated lattice energy ($E[SnO_2] = -122.32 \text{ eV}$, $E[In_2O_3] = -150.01 \text{ eV}$), we can predict the dominant mechanism of the intrinsic ionic disorder and defect formation. In Tables 4.9 and 4.10 we compare the relevant Frenkel and Schottky defects in SnO₂ and In₂O₃.

An ion that leaves its lattice site and occupies a non-interacting interstitial site will form a Frenkel defect pair, whereas Schottky disorder comprises vacancies in stoichiometric proportions. The formation energy for anion and cation Frenkel defect pairs in SnO₂ are calculated as:

$$E_{\text{Anion Frenkel}} = E\left[O_{i}^{"}\right] + E\left[V_{O}^{"}\right], \qquad (4.7)$$

$$E_{\text{Cation Frenkel}} = E\left[V_{\text{Sn}}^{\text{min}}\right] + E\left[\text{Sn}_{\text{i}}^{\text{min}}\right].$$
(4.8)

For Schottky defects, vacancies are removed in stoichiometric proportions to create a new formula unit of the compound, while for the anti-Schottky defect, one formula unit of the compound is added as stoichiometric interstitials:

$$E_{\text{Schottky}} = E\left[\mathsf{V}_{\text{Sn}}^{\text{m}}\right] + 2E\left[\mathsf{V}_{\text{O}}^{\text{m}}\right] + E\left[\mathsf{SnO}_{2}\right], \qquad (4.9)$$

$$E_{\text{Anti-Schottky}} = E[\text{Sn}_{i}^{\text{im}}] + 2E[\text{O}_{i}^{\text{im}}] - E[\text{SnO}_{2}].$$
(4.10)

According to the calculations, we find that the primary type of the intrinsic disorder is the anion Frenkel pair in SnO₂, which agrees with the prediction of Hines *et al.* [38], while Freeman and Catlow [37] found similar values for Schottky and Frankel energies, with that for the Schottky being slightly lower. Based on the lowest-energy anion and cation interstitials and vacancies, a similar conclusion can be drawn about the dominance of the anion Frenkel pair in In_2O_3 . We note that the energies of the intrinsic disorder reactions in SnO₂ are high, indicating that there will be very low levels of thermally generated defects. The Frenkel energies in In_2O_3 are somewhat lower.

4.8 Electron and Hole Reaction Energies

Defect		Defect energy per defect (eV)			
	P1	Present work	Freeman and Catlow [37]	Hines <i>et al</i> . [38]	
Anion Frenkel	6.01	6.33	5.54	7.99	
Cation Frenkel	8.34	9.26	9.63		
Schottky	5.06	7.92	5.19	11.32	
Anti-Schottky	8.51	6.69	8.61		

Table 4.9 Defect formation energy in SnO₂.

Defect		Defect energy per defect (eV)		
	P1	Present work	Walsh <i>et al.</i> [25]	
Anion Frenkel	3.62	3.67	3.19	
Cation Frenkel	7.26	7.00	6.85	
Schottky	4.82	6.16	4.44	
Anti-Schottky	5.34	3.83	4.87	

Table 4.10 Defect formation energy in In₂O₃.

4.8 Electron and Hole Reaction Energies

ITO is a solid solution, in which Sn is doped into In_2O_3 at low concentrations, under which the electronic mechanism of charge compensation dominates:

$$\ln_{\ln}^{\times} + \operatorname{SnO}_{2(s)} \to \operatorname{Sn}_{\ln}^{\cdot} + \frac{1}{2} \ln_2 O_{3(s)} + \frac{1}{4} O_{2(g)} + e'$$
 (4.11)

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

$$\ln_{\ln}^{\times} + \operatorname{SnO}_{2(s)} \to \operatorname{Sn}_{\ln}^{\cdot} + \frac{1}{2} \ln_2 O_{3(s)} + \frac{1}{2} O_i^{\prime\prime} .$$
 (4.12)

The calculated energies of reactions (4.11) and (4.12) of -2.24eV and 0.05eV, however, clearly show the dominance of the electronic disorder, which will be further discussed in the next section (see Table 4.12 below for the relevant defect energies). We have assumed O-rich conditions in the above reactions; the corresponding energies for O-poor conditions are obtained by shifting the energy downwards by 0.86 eV.

By combining the two reactions, the general reaction for the exchange of an electron in the conduction band for an oxygen interstitial is given by:

$$e' + \frac{1}{4}O_{2(g)} \rightarrow \frac{1}{2}O''_i$$
 (4.13)

Similar defect reactions can be written for both electron and hole carriers, in which they are charge compensated by ionic defects either under O-rich (cation-poor) or O-poor (cation-rich) conditions, as has been proposed in earlier studies on equilibrium between electronic and ionic defects of wide band gap materials. [155-157]

The corresponding processes and their reaction energies are listed in Table 4.11. In both materials, holes are unstable and tend to form point defects, with energies -1.32 eV for \ln_2O_3 , and -1.90 eV for SnO_2 under O-rich conditions. In contrast, electrons are stable in both SnO_2 and \ln_2O_3 , which confirms and rationalises the *n*-type nature of these materials corroborating further the methodology we have established in our previous studies on wide band-gap semiconductors. [42, 158]

Table 4.11 Reaction Energies (ΔE_f in eV) for processes, in which electron and hole carriers are charge compensated by ionic defects.

	O-rich conditions	$\Delta E_{\rm f}$	O-poor conditions	$\Delta E_{\rm f}$
SnO ₂				
Holes	$h' + \frac{1}{2}O_0^{\times} \rightarrow \frac{1}{2}V_0'' + \frac{1}{4}O_2$	-1.90	$h' + \frac{1}{2}O_0^{\times} + \frac{1}{4}Sn_{(s)} \rightarrow \frac{1}{2}V_0'' + \frac{1}{4}SnO_2$	-3.42
Electrons	$e^\prime + \frac{1}{4} O_{2(g)} \rightarrow \frac{1}{2} O_i^{\prime\prime}$	4.50	$e' + \frac{1}{4} \operatorname{Sn}_{\operatorname{Sn}}^{\times} \to \frac{1}{4} \operatorname{V}_{\operatorname{Sn}}^{\prime \prime \prime \prime} + \frac{1}{4} \operatorname{Sn}_{(s)}$	5.48
In ₂ O ₃				
Holes	$h' + \frac{1}{2}O_0^{\times} \rightarrow \frac{1}{2}V_0'' + \frac{1}{4}O_2$	-1.32	$h' + \frac{1}{2}O_0^{\times} + \frac{1}{3}In_{(s)} \rightarrow \frac{1}{2}V_0^{"} + \frac{1}{6}In_2O_3$	-2.95
Electrons	$e^{\prime}+\frac{1}{4}O_{2(g)}\rightarrow\frac{1}{2}O_{i}^{\prime\prime}$	2.29	$e' + \frac{1}{3} In_{In}^{\times} \rightarrow \frac{1}{3} V_{In}^{\prime\prime\prime} + \frac{1}{3} In_{(s)}$	5.28

4.9 Doping and Defect Cluster Formation in In₂O₃

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 8*b* and 24*d*, in Wyckoff's notation, and three interstitial sites including 8*a*, 16*c* (a lattice O site in the fluorite structure) and 24*d*. The corresponding reactions (4.11) and (4.12) for Sn substituting on the cationic sites were presented above. Alternatively, we can consider Sn

occupying on interstitial sites in In_2O_3 . Our calculation shows that, as with intrinsic interstitial defects, interstitial tin has a lower energy in the 16*c* site. These interstitial impurities can be compensated by oxygen interstitials according to (assuming O-rich conditions):

$$V_i^{\times}(In_2O_3) + SnO_{2(s)} \to Sn_i^{\dots} + 2O_i'',$$
 (4.14)

or compensated by electron carriers:

$$V_i^{\times}(In_2O_3) + SnO_{2(s)} \to Sn_i^{\dots} + 4e' + O_2.$$
 (4.15)

The energies of these reactions are, however, high at 12.08 eV and 2.94 eV, respectively (see Table 4.12 for the relevant defect energies), which should be compared with 0.05 and -2.24 eV for the reactions (4.12) and (4.11). We therefore confirm that substitutional incorporation of Sn in In_2O_3 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 spectroscopy [24] 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 $Sn_{In(b)}$ is only 0.01 eV lower than that of $Sn_{In(d)}$. Although the energy ordering we obtain agrees with experiment, the difference is so small that it cannot be the source of the observed higher *b*-site occupation.

Next, we consider formation of defect clusters involving Sn impurities in In_2O_3 , 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. While our results thus far indicate that electronic compensation is most likely, of the possible ionic species that could compensate, 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 In_2O_3 is tetrahedrally coordinated by four cations, with one *b*-site (14, 14, 14) cation and three *d*-site (x, 0, 14) cations, as shown in Figure 4.2. 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.

Table 4.12 Extrinsic defect energies and complex binding energies in In₂O₃ as well as the corresponding Wyckoff's site. We compare our results for elementary defects with those of Warschkow et al. [22]

Defect	Defect energy (eV)		Binding energy	Wyckoff's site
	Present work	Warschkow et al. [22]	(eV)	
Snin(b)	-39.35	-35.47		8b
Snin(d)	-39.34	-35.52		24 <i>d</i>
Sni	-76.94			8 <i>a</i>
Sn _i	-78.58			16 <i>c</i>
Sni ^{·····}	-76.30			24d
[OiSni]	-98.21		-3.80	
[20iSni]	-116.82		-6.59	
[30iSni] ''	-134.32		-8.27	



Figure 4.2 Interstitial oxygen in In₂O₃. In ions are represented by the larger purple spheres while O ions are represented by the smaller red spheres.

The binding energy of a cluster is calculated as the energy of the cluster less 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 4.12, while those involving

4.9 Doping and Defect Cluster Formation in In2O3

substitutional Sn, with a ratio of up to four Sn to one O are listed in Table 4.13. For each cluster type of different Sn:O stoichiometry, only the most stable combinations are given. The full range of calculation results can be found in Appendix A.

Following the notation used by Warschkow *et al.* [22], we use the symbol "•", to represent the first cationic shell and "-" for the second cationic shell. From the results in Table 4.12, we see that forming clusters between interstitial Sn and O lowers the energy significantly. We note, however, that, combining the energies of reactions (4.15) and twice that of (4.13) 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 (4.14), which compensates the interstitial Sn by two non-interacting 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 energy for the incorporation of interstitial Sn, substitutional Sn will remain the lower energy solution mode.

For clusters of nearest-neighbour Sn_{ln} and O_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 $Sn_{ln(d)}$ are at least 0.4 eV lower than the energies of clusters only including $Sn_{ln(b)}$. 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.

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 $(Sn_{In(d)} \cdot O_i)$ ', $(2Sn_{In(d)} \cdot O_i) \times$ and $(3Sn_{In(d)} \cdot O_i)^{-}$. 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

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prediction of the Sn dominant occupation of *d* sites on the cationic sublattice corroborates the report of Warschkow *et al.* [22], who also found a strong *d*-site preference; but as noted above it disagrees with the experimental Mossbauer data.

Considering defect formation energies of complexes between substitutional Sn and interstitial O, we should account for all involved reactants as shown in equations (4.16) to (4.19):

$$\ln_{\ln}^{\times} + \frac{1}{4}O_{2(g)} + e' + SnO_{2(s)} \to [Sn_{\ln}^{\cdot}O_{i}'']' + \frac{1}{2}\ln_{2}O_{3(s)}, \qquad (4.16)$$

$$\ln_{\ln}^{\times} + \operatorname{SnO}_{2(s)} \to \frac{1}{2} [2 \operatorname{Sn}_{\ln}^{\cdot} O_{i}^{\prime \prime}]^{\times} + \frac{1}{2} \operatorname{In}_{2} O_{3(s)}, \qquad (4.17)$$

$$\ln_{\ln}^{\times} + \operatorname{SnO}_{2(s)} \to \frac{1}{3} [3\operatorname{Sn}_{\ln}^{\cdot} O_{i}^{\prime \prime}]^{\cdot} + \frac{1}{2} \operatorname{In}_{2} O_{3(s)} + \frac{1}{12} O_{2(g)} + \frac{1}{3} e^{\prime} , \quad (4.18)$$

$$\ln_{\ln}^{\times} + \operatorname{SnO}_{2(s)} \to \frac{1}{4} [4 \operatorname{Sn}_{\ln}^{\cdot} O_{i}^{\prime \prime}]^{\cdot \cdot} + \frac{1}{2} \operatorname{In}_{2} O_{3(s)} + \frac{1}{8} O_{2(g)} + \frac{1}{2} e^{\prime} .$$
 (4.19)

The calculated reaction energies allow us to compare the stability of Sn in different complexes with the elementary substitutional site. We obtain 1.14, - 0.69, -1.80 and -1.87 eV for the respective reactions, which is, however, still above the Sn_{In} formation energy of -2.24 eV. From these observations, we conclude that complexation of Sn with any available interstitial O will necessarily occur in Sn doped In₂O₃ under thermodynamic equilibrium at finite levels of doping while the equilibrium, while shift towards electrons rather than oxygen interstitials as a charge compensating species.

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Sn:Oi	Defect cluster	Complex binding energy (eV)		
ratio	-	P1	Present work	Warschkow
				et al. [22]
1:1	(Sn _{in(d)} •O _i)'	-0.80	-1.54	-1.29
[Snin•Oi]'	(Sn _{In(<i>b</i>)} •O _i)'	-0.36	-1.19	-0.89
	(Snin(<i>b</i>)-Oi)'	-0.95	-0.93	-1.16
	(Snin(<i>d</i>)-Oi)'	-0.87	-0.85	-1.10
2:1	(2Sn _{In(d)} •O _i)×	-1.23	-2.64	-1.91
[2Snin•Oi]×	$(Sn_{in(b)} \bullet Sn_{in(d)} \bullet O_i)^{\times}$	-0.71	-2.26	-1.54
	$(Sn_{in(b)} - Sn_{in(d)} \bullet O_i)^{\times}$	-1.46	-2.23	-2.09
	$(Sn_{In(d)} - Sn_{In(d)} \cdot O_i)^{\times}$	-1.39	-2.15	-2.05
	$(Sn_{in(b)} - Sn_{in(b)} \cdot O_i)^{\times}$	-0.94	-1.74	-1.54
	$(Sn_{In(d)} - Sn_{In(b)} \bullet O_i)^{\times}$	-0.94	-1.73	-1.63
	$(2Sn_{ln(b)} - O_i)^{\times}$	-1.69	-1.66	-2.08
	$(Sn_{In(b)} \bullet Sn_{In(d)} - O_i)^{\times}$	-1.61	-1.58	-2.00
	(2Sn _{In(<i>d</i>)} -O _i)×	-1.49	-1.50	-1.97
3:1	(3Sn _{In(d)} •O _i) [•]	-1.21	-3.31	-1.86
[3Snin•Oi]	$(Sn_{in(b)} \bullet 2Sn_{in(d)} \bullet O_i)$	-0.67	-2.90	-1.49
	$(Sn_{In(d)} - 2Sn_{In(d)} \cdot O_i)$	-1.43	-2.89	-2.14
	$(2Sn_{In(b)} - Sn_{In(d)} \cdot O_i)$	-1.91	-2.55	-2.35
	$(Sn_{In(d)} \bullet Sn_{In(d)} \bullet Sn_{In(d)} \bullet O_i)$	-1.81	-2.44	-2.31
	$(2Sn_{In(d)} - Sn_{In(d)} \cdot O_i)$	-1.63	-2.37	-2.24
	(3Sn _{In(b)} -O _i) [•]	-2.20	-2.18	-2.55
	$(2Sn_{\ln(b)} \cdot Sn_{\ln(d)} - O_i)$	-1.91	-2.01	-2.43
	$(2Sn_{In(d)} - Sn_{In(b)} \bullet O_i)$	-1.29	-1.96	-1.88
	$(Sn_{In(b)} \bullet 2Sn_{In(d)} - O_i)$	-1.88	-1.85	-2.36
	(3Sn _{In(d)} -O _i) [•]	-1.88	-1.83	-2.33
4:1	$(Sn_{In(b)} \bullet 3Sn_{In(d)} \bullet O_i)$	-0.25	-3.12	-0.88
[4Sn _{in} •Oi]				

Table 4.13 Sn_{ln} and O_i complex binding energies in In_2O_3 . We compare our results with those of Warschkow et al. [22]

4.10 Conclusions

In this Chapter, a new set of transferable pairwise interatomic potentials for SnO₂ and In₂O₃ have been presented. 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 In₂O₃ and effects of impurity clustering, and their thermodynamic stability. Our calculations show a significant improvement, compared to older parameterisations, of lattice energies and oxygen vacancy formation energies of both SnO_2 and In_2O_3 that are in acceptable agreement with experiment and available QM/MM results [42]. 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 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 In₂O₃. The study of impurity clustering with interstitial oxygen reveals a progressive stabilisation of Sn on cluster growth, which points to a possibly increasing role of the ionic charge compensation with the level of doping in In_2O_3 .

A summary of the work reported in this chapter has been published [159] and further studies of defects in In_2O_3 using quantum mechanical methods are reported in Chapter 7.

Intrinsic point defects in ZnO

5.1 Introduction

As discussed in Chapter 1, ZnO is a wide-bandgap semiconductor with many applications including light-emitting diodes [160, 161], solar cells [162], piezoelectric devices [163] and thin-film transistors [164]. Native defects play a key role in the electrical and optical properties of ZnO, such as controlling doping, luminescence efficiency and minority carrier lifetime. Therefore, understanding the intrinsic point defects in ZnO is important for improving device applications.

The unintentional *n*-type conductivity in ZnO has been traditionally attributed to the presence of native donor defects, such as the O vacancy (Vo) and Zn interstitial (Zni). [50, 54, 165] However, most of these arguments were based on indirect evidence (*e.g.* that the electrical conductivity increases as the oxygen partial pressure decreases). Computational studies, however, indicate that the oxygen vacancy is a deep donor. [56-59, 62, 67, 166-169] Native acceptors such as the zinc vacancy (Vzn) and oxygen interstitial (Oi) are considered to be sources of electrical compensation [170] and luminescence. [97, 171, 172]

In this Chapter, Intrinsic point defects in ZnO are investigated using the hybrid QM/MM embedded cluster approach. The atomic and electronic structure, formation and ionisation energies of the point defects are determined from local minima on the potential energy landscape, which allows us to predict concentrations of point defects and carriers for a range of physically and

chemically relevant temperatures and oxygen partial pressures under thermodynamic equilibrium.

In the following section we provide methodological and technical details of the calculations.

5.2 Calculation Settings

The hybrid QM/MM embedded cluster technique (Chapter 3.2.5) is employed to calculate bulk and defect energies in ZnO. In our QM/MM model, the inner cluster of 86 atoms of wurtzite ZnO containing the central defect and its surrounding atoms is treated with a QM method. We have employed three exchange and correlation functionals: the BB1k functional [117], which has been fitted to both thermochemical and kinetic data including 42% exact exchange; the PBE0 functional [118], which is frequently used in plane-wave basis calculations including 25% exact exchange; and the B97-2 functional [119], which has been fitted to a broad range of thermochemical date with 21% exact exchange. The outer region which contains 10460 atoms is treated with the MM method using interatomic potentials [120]. The specially designed local ECP taken from Buckeridge *et al.* [42] is used on cation sites in the interface between the QM and MM regions, as given in Table 3.1.

The formation energies of defects are determined by the following reactions:

$$Zn_{zn}^{\times} \to V_{Zn}^{q^-} + Zn_{(s)} + qh^+$$
, (5.1)

$$\operatorname{ZnO}_{(s)} \to O_i^{q-} + \operatorname{Zn}_{(s)} + qh^+$$
, (5.2)

$$Zn_{(s)} \to Zn_i^{q+} + qe^-$$
, (5.3)

$$O_0^0 + Zn_{(s)} \to V_0^{q+} + ZnO_{(s)} + qe^-,$$
 (5.4)

for zinc rich/oxygen poor conditions, and

$$\operatorname{Zn}_{\operatorname{Zn}}^{\times} + \frac{1}{2} O_{2(g)} \to V_{\operatorname{Zn}}^{q-} + \operatorname{Zn}O_{(s)} + qh^{+},$$
 (5.5)

$$\frac{1}{2}O_{2(g)} \to O_i^{q-} + qh^+ , \qquad (5.6)$$

5.2 Calculation Settings

$$\operatorname{ZnO}_{(s)} \to \operatorname{Zn}_{i}^{q+} + \frac{1}{2}O_{2(g)} + qe^{-},$$
 (5.7)

$$0_0^0 \to V_0^{q+} + \frac{1}{2} O_{2(g)} + q e^-,$$
 (5.8)

for zinc poor/oxygen rich conditions.

The formation energies of Schottky defects and its their counterparts can be determined from:

$$Zn_{zn}^{\times} + O_0^0 \to V_{Zn} + V_0 + ZnO_{(s)}.$$
(5.9)

The chemical potentials of O₂ molecular and single Zn atoms are calculated using GAMESS-UK with the corresponding basis set and density functional; the standard state energy of ZnO is derived from the experimental heat of formation [49].

5.3 Ionization potential

The calculated ionization potentials (IPs) which are the energy difference between the positively charged cluster and the neutral one and are given in Table 5.1.

Europhic and	ID-
Functional	IPS
BB1k	8.26
PBE0	7.64
B97-2	7.32
Previous calculations	7.0-8.5 [81, 173-177]
Experiment	6.9-7.8[150, 178, 179]

Table 5.1 Calculated ionization potentials (eV) of ZnO.

The bulk ionization potential can be higher or lower than the surface IP but would be expected to be close for well-prepared / equilibrated experimental samples, subject to the surface band bending. Therefore, the agreement between our calculations and others in the literature and experiment is good. Of the three functionals used, BB1k results in the highest IPs, then PBE0, followed by B97-2, a trend which reflects the different accounts of electron localization in the functionals. The large calculated values of the IP position the VB deep below the vacuum level. Therefore, the hole formation energy is high, while the formation energy of the positively charged defect (*e.g.*, oxygen vacancies) will be low when the Fermi level close to the VBM, which explains the observed difficulty in p-type doping ZnO, as discussed in detail in references [155] and [157].

5.4 Compact defect states and structures

This Chapter focus on the four main intrinsic point defects of ZnO in their main charge states: (1) zinc interstitials, Zn_i, (2) oxygen vacancies, V₀, (3) zinc vacancies, V_{zn} and (4) oxygen interstitials, O_i.

The electronic states and related structures of defects are discussed. Considering the perfect lattice as a reference, a point defect is characterised by its charge and spin. Both variables (or observables) are parameters in our calculations and are controlled by the nuclear charges and the number of electrons in the QM region. The QM software of our choice (GAMESS-UK) does not allow for relaxation of these parameters in contrast to many periodic QM codes. Following conventional terminology of semiconductor physics, defects that can donate electrons to the conduction band of the host material are called donors, and those that can accept electrons from, or donate holes to the valence band are called acceptors, respectively. To determine the ability of defects to donate or accept electrons, we calculate their ionisation potentials or electron affinities with respect to the conduction or valence bands, and refer to them as donor or accepter levels. We consider that a defect state is stable, if its donor and acceptor levels are not in the conduction and valence bands, respectively, otherwise, the defect would be in a resonance state and automatically ionise.

In this section, we focus on traditional compact states of the defects, that are often termed deep (level) states. This account is complemented by the results and discussion of diffuse (so called shallow) defect states in section 5.5.

5.4.1 Zn interstitial Zn_i

The Zn interstitial is expected to be more stable at the octahedral site than at the tetrahedral site, as discussed in previous studies by Janotti and Van de Walle [58] and Sokol *et al.* [81]. Hence, we here only concentrate on the Zn interstitial at the octahedral site.

The +2 state is below the VBM by 1.37-1.71 eV which can attract electrons (In Figure 5.1, black lines denote vertical electron ionization to the conduction band

5.4 Compact defect states and structures

minimum (CBM), red lines are hole ionization to the valence band maximum (VBM) – see section 3.4.3). The neutral interstitial has a lower coordination by electron rich O^{2-} ions and forms a trigonal pyramid with the closest Zni–O separation distance of 1.99 Å and the two other distances of 2.01 and 2.02 Å (BB1k structures shown in Figure 5.2(a)). The ground state of the neutral interstitial is a singlet, for which the formation energy is 1.15 eV (B97-2), 1.14 eV (PBE0) or 1.13 eV (BB1k) lower than triplet. On ionisation this nearly symmetric configuration is broken, with the Zn⁺ ion moving towards one of the lattice oxygens (2.01, 2.06 and 2.03 Å). The next nearest O ions move now towards the interstitial Zn (by 0.30, 0.32, and 0.41 Å), but do not approach close enough to coordinate to this ion directly by a dative bond (Figure 5.2(b)). Losing the second electron results in the next nearest O ions moving towards the interstitial Zn by 0.08 Å (Figure 5.2(c)).



Figure 5.1 Optical energy levels of Zn_i in ZnO with respect to band edges, calculated using the BB1k, PBE0 and B97-2 density functional. (+2 singlet, +1 doublet, 0 singlet)



Figure 5.2 Zn interstitial at octahedral site in charge state 0 (a), +1 (b) and +2 (c) in ZnO. (BB1k structures)

5.4.2 O vacancy V₀

The +2 state of the O vacancy formed by removing an O^{2-} anion leaves no electrons remaining in the vacancy site. The positive Madelung potential of the vacancy therefore pushes occupied electronic levels around the defect below the VBM by ~1.42-1.44 eV as shown in Figure 5.3. This positively charged vacancy can trap an electron which would result in the formation of an F⁺ centre with the defect level in the band gap. The neutral state of the O vacancy is a conventional F-centre which has been identified in halide and oxide systems, where the Madelung potential trapped electrons at the anion vacancy sites. [127, 180].

For the neutral charge state, two electrons are trapped at the vacancy site, the four nearest Zn neighbours are displaced inward by 0.20-0.27 Å (Figure 5.4(a)). After removing two electrons form the vacancy, the four Zn atoms strongly relax outward by 0.21-0.23 Å as shown in Figure 5.4(c) (BB1k structures).



Figure 5.3 Optical energy levels of V_0 in ZnO with respect to band edges, calculated using the BB1k, PBE0 and B97-2 density functional. (+2 singlet, +1 doublet, 0 singlet, 1- doublet)



Figure 5.4 O vacancy in neutral (a), +1 (b) and +2 (c) charge states in ZnO. The spin density of the +1 state is indicated by isosurfaces 0.009, 0.005, 0.0025 au highlighted in yellow. (BB1k structures)

5.4.3 Zn vacancy V_{Zn}

The Zn vacancy is stable in five charge states: -2, -1, 0, +1 and +2. A missing Zn^{2+} ion leaves the -2 state of the Zn vacancy with no electrons remaining in the vacant site because the Madelung potential destabilises the electron states of cation vacancies. In contrast to the F-centre, the neighbouring O ions strongly repel each other and relax outwards.

In the -2 state, the two electrons are contributed by the original Zn ion to the VB and all nearest neighbour O ions retain their charge state -2. The four nearest neighbour O^{2-} ions which belong to the same hexagonal ZnO sheets as the vacancy relaxed outward (one along the *c*-axis by 0.43 Å, and three in the *ab* plain by 0.04, 0.09 and 0.09 Å).

In the -1 state, one of the four neighbour O ions binds a hole, forming a spin doublet. On ionisation of the -2 state, the hole localised on one of the oxygens of the hexagonal sheet (as shown in Figure 5.6) relaxed more than the other oxygen ions.

For the neutral charge state, two holes are created on the nearest neighbour O ions. These two holes can couple to total spin 0, in a diamagnetic (closed-shell singlet) or antiferromagnetic (open-shell singlet) configuration; or a ferromagnetic coupling (triplet state) is realised with spin of 1 [81]. The formation energy (see section 3.4.2) of the relaxed open-shell singlet state is 6.43 eV (B97-2), 6.96 eV (PBE0) and 7.09 eV (BB1k), which is 0.09 eV, 0.12 eV and 0.005 eV higher than the ground state triplet. The spin density in the triplet state is predominantly localised on two oxygen ions from the same hexagonal sheet (as shown in Figure 5.4(a)) which also relaxed more than the ones without the holes.

All the charge states mentioned above introduce donor energy levels in the band gap (Figure 5.5). The energy level of the neutral charge state is closer to the VBM, losing one more electron will result in the energy level of the +1 charge state, which is 0.55 eV (B97-2) or 0.55 eV (PBE0) below VBM.

5.4 Compact defect states and structures



Figure 5.5 Optical energy levels of V_{Zn} in ZnO with respect to band edges, calculated using the BB1k, PBE0 and B97-2 density functional. (-2 singlet, -1 doublet, 0 triplet, +1 doublet, +2 singlet)



Figure 5.6 Zn vacancy in 0 (a. triplet, b. singlet) -1 (c), and -2 (d) charge states in ZnO. The spin densities of the 0 and -1 state are indicated by isosurfaces of increasing transparency with three levels of ±0.1, 0.05, 0.025 eBohr³ highlighted in yellow (+) and blue (-), we will adopt the same visualisation scheme in all following figures. (BB1k structures)

5.4.4 O interstitial O_i

Two possible interstitial positions in ZnO are the octahedral and tetrahedral sites. We found that, instead of occupying either, the ground state configuration of the neutral oxygen interstitial is the split interstitial, which agrees with previous DFT calculations. [57, 58]

The octahedral oxygen interstitial is stable in three charge states: -2, -1, and 0. In the -2 state, octahedral oxygen interstitial forms a trigonal pyramid structure as shown in Figure 5.8. A neutral oxygen interstitial in the triplet state at the octahedral site remain the trigonal pyramidal structure. After being excited in a singlet state, the atom relaxes into the split interstitial position as shown in Figure 5.9 (named O split interstitial 1). The ground state electronic configuration of the neutral split oxygen interstitial is a singlet, while the neutral octahedral oxygen interstitial is a triplet. The neutral oxygen interstitial at the tetrahedral site also relaxes into the split interstitial position as shown in Figure 5.10 (named O split interstitial 2).

The O split interstitial defect, also referred to as the O dumbbell interstitial [61, 181], adopts three possible structures (1, 2 and 3) as shown in Figure 5.9, Figure 5.10 and Figure 5.11.

In the neutral O split interstitial 1 configuration which is relaxed from the octahedral configuration (Figure 5.9), the calculated O-O distance is 1.48 Å, suggesting the formation of an O-O chemical bond, that is expected for a peroxy-species. Two of the nearest Zn become 5-coordinated and their distances to the split O are 0.14 and 0.16 Å larger than the equilibrium Zn-O distance in pure ZnO. Electron trapping at the split interstitial site causes the distance between the two split oxygens to increase to 2.13 Å and the two 5-coordinated Zn to O increase by 0.06 and 0.08 Å compared to the equilibrium Zn-O distance. The O-O distance reduces to 1.32 Å when trapping a hole.

The neutral O split interstitial 2 configuration (Figure 5.10) is relaxed from the tetrahedral interstitial, with the distance between the two split oxygens of 1.43 Å. The distances from the four neighbour Zn ions to the split O are reduced by 0.03 Å compared to their normal values. In the + charge state, the O-O distance

is 1.30 Å, the Zn-O distances are 0.06 Å larger than their normal values. In the -1 charge state, the distance between the two split oxygens increases to 2.15 Å.

The neutral O split interstitial 3 configuration (Figure 5.11) can be viewed as a rotated configuration of the split interstitial 2 configuration, with the distance between the two split oxygens of 1.44 Å. The split oxygen is coordinated to two Zn ions with the distances reduced by 0.02 and 0.03 Å compared to their normal values. In the + charge state, the O-O distance is 1.31 Å, the four Zn-O distances are 0.07, 0.07, 0.10 and 0.13 Å large than their normal values. In the -1 charge state, the distance between the two split oxygens increases to 2.14 Å.

5.4 Compact defect states and structures



Figure 5.7 Optical energy levels of O_i in ZnO with respect to band edges, calculated using the BB1k, PBE0 and B97-2 density functional.

5.4 Compact defect states and structures



Figure 5.8 Oxygen interstitial at octahedral site in 0 (a) -1 (b), and -2 (c) charge states in ZnO. The spin densities of the 0 and -1 state are indicated by isosurfaces 0.1, 0.05, 0.025 au highlighted in yellow. (BB1k structures)



Figure 5.9 Oxygen split interstitial 1 in 0 (a) -1 (b), and +1 (c) charge states in ZnO. The spin densities of the -1 and +1 state are indicated by isosurfaces 0.1, 0.05, 0.025 au highlighted in yellow. (BB1k structures)



Figure 5.10 Oxygen split interstitial 2 in 0 (a) -1 (b), and +1 (c) charge states in ZnO. (BB1k structures)



Figure 5.11 Oxygen split interstitial 3 in 0 (a) -1 (b), and +1 (c) charge states in ZnO. (BB1k structures)

5.5 Diffuse defect states

To calculate the binding energies of electrons or holes using equation (3.30) - (3.32) in section 3.4.1, we take the computed value of ε (9.77) for ZnO from our interatomic forcefields, and experimental value of m^* : $m_e^* = 0.22m_e$ for electrons [42, 182, 183], and $m_h^* = 1.29m_e$ for holes [182]. The binding energy for one or two diffuse electrons (to CBM) or holes (to VBM) are summarised in Table 5.2.

electrons	Binding energy (eV)	holes	Binding energy (eV)
e _{m*} (H) for +1	-0.032	h _{m*} +(H) for -1	-0.184
e _{m*} (H) for +2	-0.127	h _{m*} ⁺ (H) for -2	-0.736
2e [*] _{m*} (He) for +2	-0.185	2h ⁺ _{m*} (He) for -2	-1.068
$2e_{m^*}$ (Hydride) for +1	-0.034	$2 h_{m^*}^+$ (Hydride) for -1	-0.194

Table 5.1 The binding energies (in eV) of the diffuse electrons and holes in ZnO.

The calculated energies of compact and diffuse defect states (see section 3.4.1) for each defect and density functional are given in Table 5.3 to Table 5.6. The energies (in eV) are given for the Fermi energy at the CBM with the electron in the CB and the hole in the VB.

5.5 Diffuse defect states

Charge state		defect		Functional	
			BB1K	B97-2	PBE0
0	compact	Zn ^o i	4.63	4.67	3.92
	diffuse	Zn [⁺] _i +e [⁺] _{m*} (H)	2.93	4.14	3.38
		Zn ²⁺ _i + 2e ⁻ _{m*} (He)	1.37	3.67	2.86
1+	compact	Zn ⁺ i	2.96	4.17	3.41
	diffuse	Zn ²⁺ _i + e ⁻ _{m*} (H)	1.43	3.73	2.92
2+	compact	Zn ²⁺ _i	1.56	3.05	3.86
	diffuse	$Zn_{i}^{+} + h_{m^{*}}^{+}(H)$	6.21	7.43	6.67

Table 5.2 The energies	(in eV) of the compact an	d diffuse state of Zniin ZnO.
	(

ble 5.3 The Energies (in eV) of the compact and diffuse state of V ₀ in ZnO.

Charge state		defect	Functional		
			BB1K	B97-2	PBE0
0	compact	V _o	0.16	-0.13	-0.09
	diffuse	V ₀ ⁺ + e _m ⁺ (H)	0.88	1.16	1.27
		V ₀ ²⁺ + 2e _{m*} (He)	0.89	1.87	1.94
1+	compact	V _o ⁺	0.91	1.19	1.30
	diffuse	$V_{0}^{2+} + e_{m^{*}}(H)$	0.94	1.93	2.00
2+	compact	V ₀ ²⁺	1.07	2.05	2.12
	diffuse	V _o + h _{m*} (H)	4.17	4.44	4.55
1-	compact	V _o	2.62	4.79	4.87
	diffuse	V_{O}^{+} + 2 $e_{m^{*}}^{-}$ (Hydride)	0.88	1.16	1.26

Table 5.4 The Fr	neraies (in e\/)	of the compa	act and diffuse	state of V_{7} in ZnO
	1019103 (111 0 1)			

Charge state		defect	Functional		
			BB1K	B97-2	PBE0
0	compact	V_{Zn}^0	7.09	6.35	6.94
	diffuse	$V_{Zn}^{-} + h_{m^{*}}^{+}(H)$	9.30	7.82	8.54
		V _{Zn} ²⁻ + 2h _{m*} ⁺ (He)	10.91	8.66	9.48
1-	compact	V _{Zn}	6.05	4.56	5.28
		V ²⁻ _{Zn} + h ⁺ _{m*} (H)	7.80	5.55	6.38
2-	2- compact		5.10	2.85	3.68
	diffuse	$V_{Zn}^{-} + e_{m^*}^{-}(H)$	6.02	4.53	5.25

5.5 Diffuse defect states

Charge state		defect		Functional			
			BB1K	B97-2	PBE0		
0	compact	O ⁰ _i (oct)	7.62	7.74	7.58		
	diffuse	$O_i(oct) + h_{m^*}(H)$	10.00	9.65	9.53		
		O ²⁻ _i (oct)+ 2h ⁺ _{m*} (He)	12.53	11.31	11.45		
0	compact	O ⁰ _i (split 1)	5.72	5.98	5.69		
	diffuse	O _i (split 1)+ h _{m⁺} +(H)	9.75	9.34	9.22		
		O_i^* (split 1)+ $e_{m^*}(H)$	6.95	7.88	7.65		
0	compact	O ⁰ _i (split 2)	5.68	5.75	5.49		
	diffuse	diffuse $O_i^{-}(\text{split 2}) + h_{m^*}^{+}(H)$		9.61	8.92		
		O_i^+ (split 2)+ $e_{m^*}(H)$	6.97	7.68	7.31		
0	compact	O ⁰ _i (split 3)	5.79	5.86	5.72		
	diffuse	$O_i(split 3) + h_{m^*}(H)$	9.62	9.20	8.93		
		O_i^* (split 3)+ $e_{m^*}(H)$	7.03	7.40	7.79		
1-	compact	O _i (oct)	6.75	6.39	6.28		
	diffuse	O ²⁻ _i (oct)+ h ⁺ _{m*} (H)	9.43	8.20	8.34		
2-	compact	O ²⁻ _i (oct)	6.73	5.50	5.64		
	diffuse	O _i (oct)+e _m ∗(H)	6.71	6.36	6.25		

Table 5.5 The Energies (in eV) of the compact and diffuse state of O_i in ZnO.

5.6 Ionization energies as defect (transition) levels

Understanding the vertical ionization potentials and electron affinities after knowing the defect formation energies of different oxidation states (charge states) and the transition levels between different charge states, can provide information on many defect processes that play a key role in light absorption and luminescence, and charge trapping. By comparing with the experimentally observed photoluminescence peaks and zero phonon lines (ZPL), the sources of defects that generate different optical signals can be identified, and the experimentally observed luminescence properties can be explained.

Configurational coordinate diagrams (CC diagram, see section 3.4.3) are used to analyse the optical properties of the defects. In this section, the calculated ionisation energies for the full range of point defects and charge states of ZnO using the BB1k functional, which is expected to provide a better account of electron localisation and more accurate ionisation energies, are summarised in Table 5.7 (compact states) and Table 5.8 (diffuse states). The B97-2 and PBE0 results are given in Table 5.9 for comparison. The resulting CC diagrams are given in section 5.7 to analyse the defect processes.

5.6 Ionization energies as defect (transition) levels

Summary of calculated ionisation energies							
Defect states			BB1k				
	Epl	E_{ab}	ZPL	E _{rel}	E _{rel} *		
V _{Zn} (-2 -1)e	-0.61	2.20	0.95	1.56	1.25		
V _{Zn} (-1 0)e	0.08	2.13	1.04	0.96	1.10		
V _{Zn} (0 +1)e	0.55	2.57	1.58	1.04	0.99		
V _{Zn} (-1 -2)h	1.24	4.05	2.49	1.25	1.56		
Vzn (0 -1)h	1.30	3.36	2.40	1.10	0.96		
V _{Zn} (+1 0)h	0.87	2.89	1.85	0.99	1.04		
V ₀ (+1 +2)e	-1.12	2.10	0.16	1.28	1.94		
Vo (0 +1)e	-0.48	2.21	0.75	1.23	1.46		
V ₀ (-1 0)e	-3.09	-2.20	-2.47	0.63	0.26		
V ₀ (+2 +1)h	1.33	4.56	3.28	1.94	1.28		
Vo (+1 0)h	1.23	3.92	2.68	1.46	1.23		
Vo (0 -1)h	5.64	6.53	5.90	0.26	0.63		
O _i (-2 -1)e	-2.03	1.37	0.02	2.05	1.35		
O _i (-1 0)e	-0.39	1.71	0.88	1.27	0.83		
O _i (0 +1)e	0.94	2.61	1.71	0.77	0.90		
O _i (-1 -2)h	2.07	5.47	3.42	1.35	2.05		
O _i (0 -1)h	1.73	3.83	2.56	0.83	1.27		
O _i (+1 0)h	0.82	2.50	1.73	0.90	0.77		
O _{i-split-1} (-1 0)e	-2.96	1.96	-0.77	2.19	2.73		
Oi-split-1 (0 +1)e	-0.21	2.62	1.26	1.47	1.37		
O _{i-split-1} (0 -1)h	1.48	6.39	4.21	2.73	2.19		
O _{i-split-1} (+1 0)h	0.81	3.65	2.18	1.37	1.47		
Oi-split-2 (-1 0)e	-2.96	2.45	-0.73	2.23	3.18		
O _{i-split-2} (0 +1)e	-0.05	2.60	1.32	1.37	1.28		
O _{i-split-2} (0 -1)h	0.99	6.40	4.17	3.18	2.23		
O _{i-split-2} (+1 0)h	0.83	3.48	2.12	1.28	1.37		
Oi-split-3 (-1 0)e	-2.99	2.45	-0.58	2.41	3.02		
Oi-split-3 (0 +1)e	0.03	2.75	1.27	1.24	1.48		
O _{i-split-3} (0 -1)h	0.99	6.42	4.01	3.02	2.41		
O _{i-split-3} (+1 0)h	0.68	3.41	2.16	1.48	1.24		
Zni (+1 +2)e	-2.33	-0.80	-1.40	0.93	0.60		
Zn _i (0 +1)e	-2.15	-1.09	-1.67	1.79	0.58		
Zn _i (+2 +1)h	4.23	5.77	4.84	0.60	0.93		
Zn _i (+1 0)h	4.53	5.58	5.11	0.58	1.79		

Table 5.6 Summary of calculated ionization energies for the full range of point defects and
charge states in ZnO by BB1k (compact states).

5.6 Ionization energies as defect (transition) lev	vels
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V _{ZnO} (+1 +2)e	0.67	3.16	2.16	1.49	1.00
V _{ZnO} (0 +1)e	0.36	2.45	1.49	1.14	0.95
V _{ZnO} (-1 0)e	-2.08	0.81	-0.85	1.23	1.66
V _{ZnO} (-2 -1)e	-3.81	-2.34	-2.97	0.84	0.64
V _{ZnO} (+2 +1)h	0.27	2.77	1.27	1.00	1.49
V _{ZnO} (+1 0)h	0.99	3.08	1.94	0.95	1.14
Vzno (0 -1)h	2.62	5.52	4.29	1.66	1.23
V _{ZnO} (-1 -2)h	5.78	7.25	6.41	0.64	0.84

5.6 Ionization energies as defect (transition) levels

Summary of calculated ionisation energies									
Defect states	BB1k								
	Epl	$E_{ m ab}$	ZPL	$E_{ m rel}$	E _{rel} *				
Vzn (-2 -1)e _{m*}	-0.64	2.20	0.91	1.56	1.28				
Vzn (-1 -2) h ⁺ _{m*}	1.05	4.05	2.31	1.25	1.74				
Vzn (0 -1) h ⁺ _{m*}	1.12	3.36	2.22	1.10	1.15				
Vo (+1 +2) e _{m*}	-1.25	2.10	0.03	1.28	2.07				
Vo (0 +1) e _{m*}	-0.51	2.21	0.72	1.23	1.49				
V _O (+2 +1) h ⁺ _{m*}	1.15	4.56	3.09	1.94	1.47				
Vo (+1 0) h ⁺ _{m*}	1.04	3.92	2.50	1.46	1.42				
O _i (-2 -1) e _{m*}	-2.07	1.37	-0.01	2.05	1.38				
O _i (-1 -2) h ⁺ _{m*}	1.89	5.47	3.23	1.35	2.24				
O _i (0 -1) h ⁺ _{m*}	1.55	3.83	2.37	0.83	1.45				
Oi-split-1 (0 +1) e _{m*}	-0.24	2.62	1.22	1.47	1.40				
Oi-split-1 (0 -1) h _m ⁺	1.30	6.39	4.02	2.73	2.37				
Oi-split-2 (0 +1) e _{m*}	-0.08	2.60	1.29	1.37	1.31				
Oi-split-2 (0 -1) h _m ⁺	0.80	6.40	3.98	3.18	2.41				
Oi-split-3 (0 +1) e _{m*}	0.00	2.75	1.24	1.24	1.51				
Oi-split-3 (0 -1) h _m ⁺	0.81	6.42	3.83	3.02	2.60				
.Zn _i (+1 +2) e [*] _{m*}	-2.46	-0.80	-1.53	0.93	0.73				
Zn _i (0 +1) e _{m*}	-2.18	-1.09	-1.70	1.79	0.61				
V _{ZnO} (+1 +2) e _{m*}	0.64	3.16	2.13	1.49	1.03				
V _{ZnO} (0 +1) e _{m*}	0.33	2.45	1.46	1.14	0.99				
V _{ZnO} (+2 +1) h ⁺ _{m*}	0.09	2.77	1.09	1.00	1.67				
Vzno (+1 0) h ⁺ _{m*}	0.80	3.08	1.76	0.95	1.32				

Table 5.7 Summary of calculated ionization energies for the full range of point defects and
charge states in ZnO by BB1k (diffuse states).

Summary of calculated ionisation energies										
Defect			B97-2					PBE0		
states	Epl	Eab	ZPL	Erel	E _{rel} *	Epl	Eab	ZPL	Erel	E _{rel} *
V _{Zn} (-2 -1)e	0.47	2.54	1.71	1.24	0.83	0.15	2.56	1.61	1.46	0.96
Vzn (-1 0)e	1.22	2.63	1.78	0.57	0.85	0.92	2.60	1.66	0.74	0.93
Vzn (0 +1)e	1.73	2.98	2.33	0.61	0.65	1.49	2.94	2.12	0.63	0.83
V _{Zn} (-1 -2)h	0.90	2.97	1.73	0.83	1.24	0.88	3.29	1.83	0.96	1.46
Vzn (0 -1)h	0.81	2.22	1.65	0.85	0.57	0.84	2.52	1.78	0.93	0.74
V _{Zn} (+1 0)h	0.45	1.71	1.10	0.65	0.61	0.49	1.95	1.32	0.83	0.63
Vo (+2 +3)e	2.26	4.86	3.59	1.33	1.27	2.07	4.88	3.54	1.46	1.35
V ₀ (+1 +2)e	-0.38	2.69	0.86	1.24	1.82	-0.38	2.70	0.83	1.21	1.87
V ₀ (0 +1)e	-1.83	2.68	1.32	3.15	1.37	-1.92	2.74	1.38	3.30	1.36
Vo (-1 0)e	-2.06	-1.28	-1.48	0.58	0.20	-2.12	-1.35	-1.52	0.60	0.17
V ₀ (+3 +2)h	-1.42	1.17	-0.16	1.27	1.33	-1.45	1.36	-0.10	1.35	1.46
Vo (+2 +1)h	0.75	3.81	2.57	1.82	1.24	0.74	3.82	2.61	1.87	1.21
Vo (+1 0)h	0.75	5.26	2.12	1.37	3.15	0.70	5.36	2.05	1.36	3.30
V ₀ (0 -1)h	4.72	5.50	4.92	0.20	0.58	4.78	5.56	4.96	0.17	0.60
O _i (-2 -1)e	-1.11	1.94	0.89	2.01	1.05	-1.27	1.81	0.64	1.91	1.17
O _i (-1 0)e	0.19	2.03	1.35	1.16	0.68	0.11	2.01	1.30	1.19	0.71
O _i (0 +1)e	1.44	3.23	2.22	0.79	1.01	1.47	3.21	2.25	0.78	0.96
O _i (-1 -2)h	1.50	4.55	2.54	1.05	2.01	1.63	4.71	2.80	1.17	1.91
O _i (0 -1)h	1.40	3.24	2.09	0.68	1.16	1.42	3.33	2.14	0.71	1.19
O _i (+1 0)h	0.21	2.00	1.21	1.01	0.79	0.23	1.97	1.19	0.96	0.78
Zni (+1 +2)e	-1.30	0.17	-0.32	0.98	0.49	-1.39	0.10	-0.37	1.02	0.47
Zn _i (0 +1)e	-2.24	-0.17	-0.50	1.79	0.33	-2.30	-0.26	-0.51	1.79	0.25
Zn _i (+2 +1)h	3.27	4.73	3.75	0.49	0.98	3.34	4.83	3.80	0.47	1.02
Zn _i (+1 0)h	3.61	5.68	3.94	0.33	1.79	3.70	5.73	3.94	0.25	1.79

Table 5.8 Summary of calculated ionization energies for the full range of point defects and
charge states in ZnO by B97-2 and PBE0 (compact states).

5.7 Defect processes

As discussed in section 2.3.4, the common luminescence bands observed in ZnO are green luminescence (GL, 2.3-2.5 eV), yellow luminescence (YL, ~2.1eV) and red luminescence (RL, ~1.8 eV) bands. The exact source of the intrinsic luminescence of ZnO due to native defects is still controversial.

In this section, the relationship between the intrinsic point defects and GL, YL and RL is analysed. The calculated defect ionisation energies and the defect energy levels for the intrinsic point defects of ZnO can be used to compare with the experimental spectroscopy data. As in our previous work [42, 128], the BB1k functional is expected to provide a better account of electron localisation and more accurate ionisation energies, therefore, this section mainly focuses on the calculated results of the BB1k functional. The problem of conventional hybrid functionals using lower than 40% fraction of the HF exchange is insufficient localisation of a hole on the anionic sublattice of ionic and, more generally, heteropolar materials, which leads to a delocalisation of a hole over multiple centres in contradiction with experiment.

The configuration-coordinate diagrams (see section 3.4.3) for four main intrinsic point defects of stable both compact and diffuse states are shown in Figure 5.12 (Zn interstitials), Figure 5.13 (O vacancies), Figure 5.14 (Zn vacancies) and Figure 5.15 (O interstitials), which shows not only the optical transitions, but also electrical processes, as interactions of defects with charge carriers.

Taking the O vacancy as an example (Figure 5.13), we firstly plot the ground state defect Vo^0 as an approximately parabolic curve. Based on the calculated E_{PL} , E_{ab} , ZPL, E_{rel}^* and E_{rel} (Table 5.7 and 5.8), the Vo^+ and Vo^{2+} are determined. When the E_{ab} is positive (arrow up) and E_{PL} is negative (arrow up), there will be a cross point.

For the hydrogenic states in the diagram, it is convenient to consider a process of an ionisation in which charge carriers are lost to the band and as the defect core relaxes to its ground state (potential energy minimum), one or more charge carriers might get trapped leading to the formation of diffuse states
(hydrogenic, helium- or hydride-like). The corresponding diagram therefore would show the diffuse states lying below the potential energy minimum of the compact state around the equilibrium and crossing the energy curve (parabola) above the potential energy minimum of the state we ionise.

5.7.1 Zn interstitial Zn_i

From the optical energy levels of the Zn interstitial as shown in Figure 5.1, we know that only +2 charge state is stable. The negative values of E_{PL} we calculate for the neutral and positively charged states of Zn_i (Table 5.9) indicate the non-radiation characteristics of the involved processes and the corresponding bounds on the thermal activation energies are rather wide.

Look and Hemsky [55] reported that high energy electron irradiation in ZnO produces shallow donors at about 25-35 meV under the CB. Because the production rate is much higher for Zn-face (0001) than O-face ($000\overline{1}$) irradiation, it has been concluded that this native shallower donor is related to a Zn-sublattice defect, probably the interstitial Zn_i or a Zn_i related complex. We did not obtain such shallow Zn_i donors as stable defects.

By thermal deep-level transient spectroscopy (DLTS) and Fourier transform infrared photocurrent (FTIR-PC) spectroscopy of ZnO thin films grown by pulsed-laser deposition (PLD), Frenzel *et al.* [184] observed commonly intrinsic deep defects E1 at 0.11 eV and E3 at 0.32 eV. By studying the behaviour of the peaks after thermal treatment, E1 is assigned to the first ionization level of Zn interstitial and E3 to the second ionization level of Zn interstitial. Brauer *et al.* [185] also assigned the E3 (0.31 eV) to the second ionization level of Zn interstitial. In contrast to Frenzel *et al.*, Mtangi *et al.* [186, 187] studied the electrical properties of single crystal ZnO anneals in hydrogen, oxygen and argon atmosphere using deep-level transient spectroscopy (DLTS). The concentration of the E1 peak (0.12 eV) increased for O₂ annealed sample and decreased after Ar and H₂ annealing, which suggests that it is a Zn vacancy related or an oxygen interstitial related defect.

The sum of first and second ionization energy of neutral state of Zn_i with two diffuse electrons, in contrast, is calculated to be 0.185 eV, which is in

agreement with the admittance spectroscopy measurements by Cordaro *et al.* [188]. They detected two donor levels T1 and T2 at ~0.17 and ~0.32 eV and related them to the second ionization of the Zn interstitial and the ionized oxygen vacancy.

We calculated the first ionization energy of neutral state of Zn_i with two diffuse electrons at 0.058 eV in agreement with Hall effect studies. Hutson [189] has measured the Hall coefficient and the electrical conductivity of single crystals of ZnO and reported that the ionization energy is 0.051 eV for both hydrogen donors and zinc interstitial donors.



Configuration coordinate

Figure 5.12 Configuration-coordinate diagram for optical transitions involving the Zn interstitial in ZnO.

5.7.2 O vacancy V₀

As discussed in section 2.3.4, GL is the most commonly observed emission in ZnO which has been the most controversial topic. Some studies assign the green luminescence to the recombination of a hole with a singly ionised oxygen vacancy V_0^+ . [84, 86, 87, 190-192] Figure 5.13 shows our calculated configuration coordinate diagram for oxygen vacancies. We determine the emission peak for hole capture by the +1 states of V_0 at 1.33 eV above the VBM, which is therefore not responsible for the green emission.

In contrast, we calculate the emission peak for hole capture by a negatively charged donor-acceptor pair (DAP) complex Vo-Vzn at 2.62 eV (Table 5.9), which is consistent with being the source of the blue luminescence. Studenikin and Cocivera [193] also assigned the change in PL colour from green to blue to a singly ionized oxygen vacancy with a zinc vacancy capture a hole.

Deep levels that have been observed in ZnO are the defects E1, E2, E3 and E4 having thermal activation energies about 0.11-0.12, 0.10, 0.29-0.32 or 0.53-0.57 eV, respectively. [194, 195] The origin of the E3 has often been explained as a structural defect, either Zn interstitial or O vacancy, or transition metal ions. Our calculations show that the E3 peak cannot be assigned to transitions solely involving the O vacancy or the Zn interstitial.



Figure 5.13 Configuration-coordinate diagram for optical transitions involving the O vacancy in ZnO.

5.7.3 Zn vacancy V_{Zn}

Here we will focus on the neutral and negative charge states of zinc vacancies as the optical transitions of positively charged zinc vacancies require V_{2n}^2 to trap 3-4 holes rapidly, which is almost impossible unless the hole concentration is extremely high. The emission peak for capture of a hole by the -2 charge state is at 1.24 eV as shown in Figure 5.14, which is close to the 1.40 eV reported by Frodason *et al.* [196], but lower than the isolated Zn vacancy emission at ~1.6 eV reported by Dong *et al.* using depth-resolved cathodoluminescence spectroscopy combined with positron annihilation spectroscopy (PAS). [197] As the valence band and the defect state have O 2*p* character, this is a *p-p* transition which should be forbidden. However, this transition may be allowed because of the large lattice relaxation, as occurs for hole capture by V_{Ga}^3 in GaN. [198]

Evans *et al.* [199] reported that the threshold energy to excite an electron from negatively charged V_{Zn} to the CB is ~2.5 eV by photo-EPR. Frodason *et al.* [196] calculated the E_{ab} of 2.67 eV for V_{Zn}^{i} using HSE. We calculate the E_{ab} of the negatively charged V_{Zn} is 2.13 eV, which is lower than previous experimental and computational values.



Figure 5.14 Configuration-coordinate diagram for optical transitions involving the Zn vacancy in ZnO.

5.7.4 O interstitial O_i

The OL and RL emissions at 1.9–2.1 eV is commonly attributed to the presence of excess oxygen, although other hypotheses such as Li dopants [200, 201] have been proposed.

Studenikin *et al.* [98] found that orange PL films can be obtained without doping the film with lithium and the OL was narrower than the one obtained from the lithium doped sample. They observed GL from oxygen deficient samples prepared by reductive annealing in forming gas and OL from oxygen rich films obtained by oxidative annealing. Wu *et al.* [99] also observed the OL disappeared and GL appeared due to the deficient of oxygen in the reducing atmosphere. They attributed the orange emission to oxygen interstitials. By annealing the ZnO nanowire arrays in reducing atmospheres, Greene *et al.* observed reduction of the OL which also confirmed the assignment of OL to oxygen interstitials.[202]

From our calculations as shown in Figure 5.15 and 5.16, we find the emission peak for capture of a hole by the -2 charge state O_i at the octahedral site is 2.07 eV which is the source of the red emissions.



Figure 5.15 Configuration-coordinate diagram for optical transitions involving the O interstitial at octahedral site in ZnO.



Figure 5.16 Configuration-coordinate diagram for optical transitions involving the O interstitial at split sites in ZnO.

In summary, we assign the blue luminescence to the emission peak for hole capture by the negatively charged V_0-V_{Zn} complex, the red luminescence to the emission peak for hole capture by the -2 charge state O_i at the octahedral site. The Assignment of calculated ionization energies to previous experimental electrical properties are summarised in Table 5.10.

 Table 5.9 Assignment of Calculated ionization energies of intrinsic point defects in ZnO using the BB1k hybrid functional to previous experimental electrical properties.

Measurement	Donor levels	Experimental	Our assignment
	(eV)	assignment	
Admittance	~0.17 (T1)	the second ionization of the	the sum of first and
spectroscopy		Zni	second ionization
[188]			energy of Zni with two
			diffuse electrons
	~0.32 (T2)	ionized Vo	not observed
DLTS [184]	0.11 (E1)	the first ionization of Zni	not observed
	0.32 (E3)	the second ionization of Zni	not observed
DLTS [185]	0.31 (E3)	the second ionization of Zni	not observed
DLTS [186, 187]	0.12 (E1)	V _{Zn} or O _i	not observed
	0.30 (E3)	Transition metal ions	not observed
Hall-effect [55]	0.025-0.035	Zni	not observed
Hall-effect [189]	0.051	Zn _i and H	the first ionization of Zn_i

5.8 Defect and charge carriers under thermodynamic equilibrium

5.8.1 Formation energies

Diagrams of the calculated formation energies are shown in Figure 5.17 as a function of the Fermi energy for point defects in ZnO under oxygen rich and poor conditions that are conventionally used to illustrate thermodynamic defect transition levels. The calculated defect formation energies of point defects in ZnO are summarised in Table 5.11.



Figure 5.17 Formation energy of point defects in ZnO as a function of Fermi level relative to the valence band maximum (VBM) under Zn-rich and O-rich conditions.

Charge	Multiplicity	B	31k	BS)7-2	PE	BE0
state	states						
		O rich	O poor	O rich	O poor	O rich	O poor
Vo							
+2	singlet	-2.10	-5.80	-1.12	-4.82	-1.05	-4.75
+1	doublet	1.18	-2.52	1.46	-2.25	1.56	-2.14
0	singlet	3.86	0.16	3.57	-0.13	3.62	-0.09
0	triplet	6.86	3.15	6.19	2.49	6.30	2.60
-1	doublet	9.77	6.06	8.49	4.79	8.57	4.87
-1	quartet	N/D	N/D	11.46	7.76	11.62	7.92
Vzn							
-2	singlet	8.27	11.98	6.02	9.73	6.85	10.55
-1	doublet	5.78	9.48	4.30	8.00	5.02	8.72
0	singlet	3.38	7.09	2.73	6.43	3.25	6.96
0	triplet	N/D	N/D	2.64	6.35	3.24	6.94
+1	doublet	1.53	5.23	1.54	5.24	1.92	5.63
+1	quartet	N/D	N/D	1.53	5.23	2.12	5.83
+2	singlet	0.41	4.12	0.95	4.65	1.34	5.05
+2	triplet	N/D	N/D	1.53	5.23	1.73	5.44
+2	quintet	N/D	N/D	0.97	4.67	1.36	5.06
Oi							
-2	singlet	9.90	13.60	8.69	12.37	8.81	12.51
-1	doublet	6.48	10.18	6.13	9.83	6.01	9.71
0	singlet	N/D	N/D	4.59	8.29	3.99	7.69
0	triplet	3.92	7.62	4.04	7.74	3.87	7.58
+1	doublet	N/D	N/D	3.59	7.30	2.99	6.69
+1	quartet	2.19	5.89	2.83	6.53	2.68	6.390
Oi_split1							
-1	doublet	6.23	9.93	5.82	9.53	5.70	9.41
0	singlet	2.02	5.72	2.28	5.98	1.99	5.69
+1	doublet	-0.16	3.54	0.77	4.47	0.54	4.24
O _{i_split2}							
-1	doublet	6.14	9.85	5.64	9.35	5.40	9.10
0	singlet	1.97	5.68	2.05	5.75	1.78	5.49
+1	doublet	-0.14	3.56	0.57	4.27	0.21	3.91

Table 5.10 Calculated defect formation energies of intrinsic point defect in ZnO.

O _{i_split3}							
-1	doublet	6.10	9.80	5.68	9.38	5.41	9.12
0	singlet	2.09	5.79	2.16	5.86	2.02	5.72
+1	doublet	-0.08	3.63	0.68	4.38	0.30	4.00
Zni							
+2	singlet	-1.61	-5.31	0.69	-3.02	-0.12	-3.83
+1	doublet	3.23	-0.48	4.44	0.74	3.68	-0.02
0	singlet	8.34	4.63	8.38	4.67	7.63	3.92
0	triplet	9.47	5.76	9.52	5.82	8.76	5.06
V _{ZnO}							
+2	triplet	0.11	0.11	0.24	0.24	0.84	0.84
+2	singlet	N/D	N/D	N/D	N/D	0.95	0.95
+1	doublet	1.38	1.38	1.03	1.03	1.80	1.80
0	singlet	3.32	3.32	2.23	2.23	3.12	3.12
0	triplet	N/D	N/D	4.41	4.41	5.19	5.19
-1	doublet	7.61	7.61	5.85	5.85	6.69	6.69
-2	triplet	14.02	14.02	11.19	11.19	12.13	12.13

We find that V₀ is the most favourable native point defect for Fermi energies within the band gap under Zn-rich conditions. The V₀ is a deep donor of a negative *U* type for Fermi energies throughout the band gap, stabilising in the +2 charge state when the Fermi energy is above the valence band maximum (VBM) with a transition to the neutral state at the Fermi level of 2.35 eV. The formation energy of V₀²⁺ near the VBM is negative, indicating a spontaneous formation, which will suppress positive free charge carriers, or holes.

For the neutral oxygen vacancy (Table 5.12), the formation energy of PBE0 (3.62eV) in O-rich conditions agree well with Alkauskas and Pasquarello [203] who reported 3.57 eV using the PBEh-32 functional. While the 3.86 eV formation energy in BB1k is closer to the 4.1 eV found by Clark *et al.* [166], who used the local density approximation (LDA) with a Thomas-Fermi screened exchange (sX) and a similar result of Oba *et al.* [66] obtained using HSE, but ~1 eV lower than the LDA values reported by Erhart *et al.* [60, 61]

The calculated (+2/0) charge transition level of 2.33 eV for PBE0 above the VBM agree with the value of 2.38 eV obtained by Alkauskas and Pasquarello [203], the ~2.4 eV by Agoston *et al.* [153] who also used PBE0 and 2.3 eV by Clark *et al.*. [166] However, with BB1k, the (+2/0) charge transition level is significantly shallower (2.98 eV above the VBM) than that of PBE0, which is surprisingly close to the 3eV reported by Zhang *et al.* [167] from their LDA calculations.

	$E_f(V_0^0)$ (O-rich)	$E_f(V_0^0)$ (O-poor)	ε (+2/0)
BB1k	3.86	0.16	2.98
PBE0	3.62	-0.09	2.33
sX [166]	~4.1	0.85	2.3
CorrLDA+U [56, 58, 59]	7.22	3.72	2.2
LDA [61]	~5.0	0.9	0.7
LDA [167]	4.6	1.5	3
CorrLDA [167]	5.5	2.4	4
GGA+ <i>U</i> [60]	~5.1	1.71	~1.2
HSE [66]	~4.1	~1	~2.4

Table 5.11 Calculated formation energies of neutral oxygen vacancies in ZnO in O-rich and Zn-rich conditions and (+2/0) thermal transition levels with respect to the VBM, compared with previous calculations using a variety of functionals.

The V_{Zn}, as an important compensating defect in *n*-type ZnO, is a double acceptor. Under oxygen-rich/Zn-poor conditions, the doubly negatively charged Zn vacancy V_{Zn}^{2-} is the dominant defect type when the Fermi level is close to the CBM with a low formation energy of 1.40 eV (BB1k) and -0.03 eV (PBE0) at the CBM.

The level of (0/-) lies at 1.78 eV (PBE0) or 2.40 eV (BB1k) above the VBM, and (-/-2) level at 1.83 eV (PBE0) or 2.49 eV (BB1k), which are closer to the CBM compared to previous studies as shown in Table 5.13. This is due to the higher formation energies calculated for negatively charged defects.

	€ (0/-)	ε (-/-2)
BB1k	2.40	2.49
PBE0	1.78	1.83
sX [166]	0.7	2.3
CorrLDA+U [56, 58, 59]	0.18	0.87
LDA [61]	-0.1	0.1
LDA [167]	-0.4	0.1
CorrLDA [167]	-0.5	0.0
GGA+ <i>U</i> [60]	~0.3	~1.1
HSE [66]	~0.7	~2.6
HSE06 [196]	1.40	1.96

 Table 5.12 Thermal transition levels of zinc vacancies in ZnO with respect to the VBM, compared with previous calculations using a variety of functionals.

The ground state configuration of the neutral oxygen interstitial is the split interstitial $O_{i(split)}$ instead of the octahedral site, which agrees with previous DFT calculations. [57, 58] Among three oxygen split interstitial configurations, the most stable is the oxygen split interstitial-2 with the formation energy of neutral state $O_{i(split2)}^{0}$ at 1.97 eV (BB1k), which is 0.05 eV lower than that of $O_{i(split2)}^{0}$ is 1.97 eV (BB1k), which is 0.05 eV lower than that of $O_{i(split2)}^{0}$ is 1.95 eV (BB1k) lower than that of $O_{i(split3)}^{0}$. The formation energies of $O_{i(split2)}^{0}$ is 1.95 eV (BB1k) lower than that of $O_{i(oct)}^{0}$. The O interstitial is a deep acceptor when occupying the octahedral site, with transition levels $\varepsilon(-/2-)$ at 2.80 eV (PBE0) and 3.42 eV (BB1k), and $\varepsilon(0/-)$ at 2.14 eV (PBE0) and 2.56 eV (BB1k) above the VBM, which agree with the results of Lyons *et al.*. [67]

The Zn_i is most stable in a +2 charge state for Fermi energies just above the VBM. This defect, however, remains a donor for Fermi energies spanning the whole band gap: the Zn interstitial will always donate its electrons to the conduction band, acting as a shallow donor.

5.8.2 Charge carrier and defect concentrations

The self-consistent Fermi energy and equilibrium defect and carrier concentrations can be determined from the computed formation energies presented in Chapter 5.4 using a Fortran code 'SC-FERMI", as introduced in Chapter 3.4.4. [129] The computed self-consistent E_F and equilibrium carrier and defect concentrations in ZnO as a function of T are shown in Figure 5.18. The range of temperatures is 0-1500 K, which encompasses common synthesis temperatures of ZnO and a majority of device operational temperatures.



Figure 5.18 The calculated self-consistent Fermi energy (*E_F*, relative to the VBM, black line) and equilibrium concentrations of electrons (*n₀*, red line), holes (*p₀*, blue line), oxygen vacancies ([*V₀*], green line), oxygen interstitials ([*O_i*], purple line), zinc interstitials ([*Z_n*], dark yellow line), zinc vacancies ([*V_{zn}*], cyan line), oxygen split interstitials ([*O_i*], brown line), zinc-oxygen vacancy complexes ([*V_{zn}*], orange line) in *Z*nO as a function of temperature, determined using the BB1k hybrid density functional, under O-poor and O-rich conditions.

Under O-rich conditions, E_F remains deep in the band gap, between 1.58 and 1.25 eV below the CBM. The carrier concentrations remain below 10^{15} cm⁻³ for T \leq 1500K for PBE0 and B97-2 functionals. When using the BB1k functional, the [Vo] is higher than that calculated using the other functionals as the transition level is shallower, meaning that the formation energy is lower at the self-consistent E_F . This concentration of oxygen vacancies in the 2+ charge state results in an excess of electrons (which remains below 10^{16} cm⁻³ for T \leq 1500K).

For O-poor conditions, the calculated $E_f(V_0)$ are significantly lower than those of other DFT studies. From such a low formation energy, we determine very high [V_0] of the order of 10^{21} cm⁻³ for T > 500K. The n_0 is 1.68×0^{18} cm⁻³ for T = 827K which is in good agreement with that determined by Halliburton *et al.* [204] who reported the electron concentration of $1.5*10^{18}$ cm⁻³ for samples treated at 827K under Zn-rich conditions.

We then investigated the equilibrium carrier and defect concentrations in ZnO as a function of the O partial pressure percent at 300K and 1000K (Figure 5.19).

To compare our results to experiment, it is important to relate the theoretically defined O-rich and O-poor condition to the oxygen chemical potential under different temperature and partial pressure conditions. Following the method by Reuter and Scheffler [205], the chemical potential of oxygen at varying oxygen partial pressures at a given temperature can be calculated as:

$$\mu_{0}(T,p) = \mu_{0}(T,p^{0}) + \frac{1}{2}kT\ln\frac{p}{p^{0}}.$$
(5.10)

By setting the zero state of $\mu_0(T, p)$ to be the total energy of oxygen at T=0 K, which is $\mu_0(0K, p^0)=(1/2)E_{02}^{\text{total}}=0$, the temperature dependence of oxygen chemical potential at a constant oxygen pressure p^0 is defined as:

$$\mu_0(T, p^0) = \frac{1}{2} [H(T, p^0, O_2) - H(0K, p^0, O_2)] - \frac{1}{2} T[S(T, p^0, O_2) - S(0K, p^0, O_2)].$$
(5.11)

where *H* is the enthalpy and *S* the entropy. Based on the data from thermochemical tables [206], $\mu_{O}(T, p^{0})$ was calculated from 100 to 1500 K by Taylor *et al.* [207] and Reuter and Scheffler [205] and is shown in Table 5.14.

Temperature /K	μ _O (T, <i>p</i> ⁰) /eV	Temperature /K	µ _O (T, <i>p</i> ⁰) /eV
100	-0.08eV	900	-0.9738eV
200	-0.17eV	1000	-1.0990eV
300	-0.27eV	1100	-1.2712eV
400	-0.38eV	1200	-1.3998eV
500	-0.50eV	1300	-1.5300eV
600	-0.6109eV	1400	-1.6617eV
700	-0.7295eV	1500	-1.7948eV
800	-0.8505eV		

Table 5.13 $\mu_0(T, p^0)$ in the temperature range of 100 to 1500 K at $p^0=1$ atm in ZnO.

The equilibrium carrier and defect concentrations in ZnO as a function of the O partial pressure from 10^{-22} to 1 atm at 1000K are shown in Figure 5.19.

Unlike Zhao *et al.* [208] who reported that ZnO exhibits weak *n*-type behaviour at low oxygen pressures and strong *p*-type at high oxygen pressures, we find that ZnO is strong *n*-type with electron concentration greater than hole concentration at high temperature and oxygen partial pressures. [Vo] is the most dominant defect in ZnO under low O partial pressures, which agrees with the work of Tomlins *et al.* [209], which supports the predominance of oxygen vacancies at low O partial pressures.



Figure 5.19 The equilibrium concentrations of electrons (n₀, red line), holes (p₀, blue line), oxygen vacancies ([V₀], green line), oxygen interstitials ([O_i], purple line), zinc interstitials ([Zn_i], yellow line), zinc vacancies ([V_{Zn}], cyan line dark), oxygen split interstitials ([O_i], brown line), zinc-oxygen vacancy complexes ([V_{Zn_0}], orange line) in ZnO as a function of oxygen partial pressures, determined using the BB1k functional under 1000K.

5.9 Summary and Conclusion

We have investigated the structures, compact and diffuse states, ionization energies, defect processes, formation energies and charge carrier and defect concentrations of the intrinsic point defects in ZnO from embedded calculations.

By calculating formation energies of each defect in different charge states, oxygen vacancies are found to be the favourable defect in O-poor/Zn-rich conditions as a deep donor of a negative *U* type for Fermi energies throughout the band gap. Under O-rich/Zn-rich conditions, the dominate defect type switches from oxygen vacancies to zinc vacancies when the Fermi level is close to the conduction band. Zinc vacancies are stable in five charge states, while the Zn interstitial at the octahedral site is only stable in the +2 charge state and remains a donor for Fermi energies across the band gap. The ground state of the neutral O interstitial is the split interstitial, which is stable in three configurations, with the formation of an O-O chemical bond.

It is proposed that the neutral state of Zn interstitial defect is responsible for T1 donor level from the admittance spectroscopy measurements. The emission peak for hole capture by negatively charged Vo-Vzn complex will be the source of the blue luminescence. Oxygen interstitials at the octahedral site contribute to the experimentally observed red luminescence. Oxygen vacancies are found to be the dominate defects from the analysis of the self-consistent Fermi energy and equilibrium defect and carrier concentrations. In 2000, copper, the most abundant impurity in ZnO, was confirmed by experiment to be a prominent source of GL in this material.[169] All recent *ab initio* studies [210] agree that Vo is not responsible for GL. In our view, if the remaining source of GL is in the bulk of the material, it must be associated with some still unknown defect complex(es).

Lithium and hydrogen impurities in ZnO

6.1 Introduction

Undoped ZnO exhibits unintentional *n*-type conductivity which has been traditionally related to the observed sub-stoichiometry of ZnO and the presence of native donor defects. [50, 54, 165] However, to realise optoelectronic devices, it is important to make *p*-type ZnO which cannot be achieved via intrinsic doping. It has been argued that high concentrations of donor impurities in ZnO may compensate acceptors or give free electrons to the conduction band, which prevent *p*-type conductivity. [211] Following the earlier work by Catlow *et al.* [155-157], in section 5.8, we have shown that the fundamental difficulty with *p* doping on ZnO arises from the instability of holes with respect to oxygen vacancies. Therefore, it is important to understand the role of impurities in ZnO. Among a large number of candidates, lithium in group I species has received particular attention.

Li is known to act as a major impurity in ZnO growth. [212] However, the location of the acceptor level of Li substitutional Zn (Lizn) remains controversial. Theoretical studies [75-77, 213] predicted Lizn to be a shallow acceptor due to the reduction of strain around the Li and coupling between the anion and cation orbitals. However, substitutional doping of Li remains difficult as lithium is very mobile and may also be located at an interstitial site as a shallow donor. Substitutional Li acceptors might therefore be self-compensated by coexisting Li interstitials. Experimental work using cathodoluminescence (CL),

6.1 Introduction

photoconductivity (PC) and Hall-effect measurements reported acceptor state among 150 meV- 260meV. [78, 79]

In contrast, instead of introducing a shallow level, other calculations [76, 80, 81] reported Li_{Zn} to be a deep acceptor, which is in agreement with experiment. [82] The Li acceptor level is at least 500 meV above the valence band and optically detected magnetic resonance (ODMR) showed that radiative recombination occurs with a deep state. [83]

Hydrogen is often present in the crystal growth environment, and it is difficult to avoid its incorporation into the crystal during the crystal growth process. As an inherent impurity in ZnO, hydrogen impurities can have a strong effect on electrical properties. It is, therefore, necessary to understand the characteristics of hydrogen species in ZnO, not only from an academic point of view, but also for semiconductor applications.

Hydrogen in ZnO, in both interstitial and substitutional forms, acts as a shallow donor in positive charged states, reported by first-principles calculations. [214] The hydrogen impurity supposedly contributes to *n*-type conductivity in ZnO.

Hydrogen can also form complexes with acceptor dopants and cation vacancies. It has been found that intentional co-doping of Li with H impurities suppressed the formation of compensating interstitials, and greatly improves the solubility of Li acceptors by forming H-acceptor complexes. [75]

In this Chapter, we report the properties of Li and H in both substitutional and interstitial forms and their complexes in ZnO using the QM/MM embedded cluster approach. We have employed three exchange and correlation functionals, B97-2, PBE0 and BB1k functionals. Calculation settings are the same as those discussed in Chapter 5.2.

6.2 Li-related defects

6.2.1 Li substituting for Zn

The formation energies of the Li substitutional are determined by following reactions:

$$\operatorname{Li}_{(\mathrm{s})} + \operatorname{Zn}_{\mathrm{zn}}^{\times} \to \operatorname{Li}_{\mathrm{Zn}}^{q^{-}} + \operatorname{Zn}_{(\mathrm{s})} + q \mathrm{h}^{+}, \qquad (6.1)$$

under Zn-rich/ O-poor conditions.

In the singly negative charged state, the distance from Li to the axial O is 1.874 Å, and to the three nonaxial O the distances are 1.895, 1894 and 1.909 Å (using the BB1k functional). After binding a hole, the charge neutral state Li⁰_{2n} is formed, with the O ion trapping the hole and with the Li ion moving from their perfect lattice position. There are two structural forms of $\mathsf{Li}_{2n}^{\scriptscriptstyle 0}$: axial and nonaxial. In the axial defect, the hole introduced by Li is fully localised on the axial O, using BB1k shown in Figure 6.1, while for B97-2, the hole is localised mainly on the axial O but also spreads to neighbouring O ions. As the BB1k functional is expected to provide a better account of electron localisation, we here focus on the structures optimised using the BB1k functional. The distance from the Li substitutional to the axial O increases by 0.271 Å, which is in agreement with experiment [215] and the calculations by Carvalho et al. [80] using hybrid density functional (HDF) based on the PBE0 form and 32% of the HF exchange. However, the Li-O bond elongation in our calculation is 14.5% which is less than that previously reported by Schirmer [215] of 40% and by Carvalho et al. [80] of 36%. Indeed, our results differ from several previous calculations. Wardle et al.[213] reported a Li-O distance of 1.92 Å without giving the hole's location. Carvalho et al. [80] reported a Li-O distance for both the axial and nonaxial bonds of 2.01 Å using PBE with the hole distributed on four neighbouring oxygens. Again, without reporting the location of the hole, the B3LYP calculation of Hu and Pan [216] gives a Li-O distance of 1.99Å. The axial defect form was found by Schirmer [215] to be more stable than the

6.2 Li-related defects

nonaxial, from analysis of the experimental results, suggesting the unpaired hole is stabilised at the axial O site as also found in our calculations.

The calculated formation energies of Lizn are plotted in Figure. 6.2. From the optical energy level results (Figure 6.3), we found Lizn is stable in neutral and negative charge states. The (-1/0) transition level of Lizn is found to lie at 0.79 eV (B97-2) from the valence band, which yields a deep acceptor level, which is in agreement with previous calculations of Sokol *et al.* [81] who reported 0.81 eV using B97-1 and Carvalho *et al.* [76, 80] who reported the transition level at 0.82 eV using HDF. Our results contrast with those of Lee and Chang [75, 76] who reported 0.04 eV, and Wardle *et al.* [213] who reported 0.25 eV, both using LDA method which suffers the consequences of its well-known underestimation of the band gap and delocalisation of the hole states. This deep acceptor level also agrees well with the electron spin resonance (ESR) results, suggesting an acceptor state of about 0.8 eV above the VBM.[95] Rauch *et al.* [217] also reported a deep Lizn acceptor state at 0.8 eV above the VBM identified in both EPR and PL. The computed $\varepsilon(-1/0)$ using BB1k is however deeper (at 1.50 eV) than that obtained using B97-2 and PBE0 as shown in Figure 6.2.

Defect	Charge state	Formation energy (eV)			
		B97-2	PBE0	BB1k	
Lizn	0	1.35	1.64	1.78	
	-1	2.14	2.49	3.28	
	-2	7.16	7.67	9.30	

Table 6.1 Calculated defect formation energies of Li_{Zn} in ZnO with the Fermi level at the VBM under Zn-rich conditions.



Figure 6.1 Li substitutional in -1 and 0 charge states in ZnO. The spin density of the neutral state is indicated by isosurfaces 0.1, 0.05, 0.025 au highlighted in yellow.



Figure 6.2 Formation energy of Li_{Zn} in ZnO as a function of Fermi level relative to the valence band maximum (VBM) under Zn-rich conditions.



Figure 6.3 Optical energy levels of Li_{Zn} in ZnO with respect to band edges, calculated using the BB1k, PBE0 and B97-2 density functional.

6.2.2 Li interstitial

Alternatively, Li may occupy an interstitial site. As mentioned in Chapter 5.4, there are two possible interstitial sites in ZnO, octahedral and tetrahedral. Hence, for the Li interstitial, both octahedral and tetrahedral sites are calculated.

The formation energy of the Li interstitial is determined by the following reaction under Zn-rich/ O-poor conditions:

$$\text{Li}_{(s)} \to \text{Li}_{i}^{q+} + q e^{-}$$
. (6.2)

The calculated formation energies of Li interstitials are shown in Table 6.2 and plotted in Figure 6.4. The formation energy of the Li interstitial in the +1 charge state Li¹⁺ at the octahedral site (Oct) is -4.74 eV (BB1k), which is 0.8 eV lower than that at the tetrahedral site (Tet). The difference with B97-2 is 0.69 eV. The energy differences for both functionals are higher than the 0.54 eV reported by Lee and Chang [75], and lower than the 0.9 eV reported by Wardle *et al.* [213], both using the LDA method.

In the neutral charge state, the formation energy of the Li interstitial Li_i^0 at the octahedral site is 0.83 eV (BB1k) or 0.78 eV (B97-2) lower than at the tetrahedral site, which is higher than the energy difference 0.62 eV reported by Carvalho *et al.* [80] and slightly lower than the 0.9 eV by Wardle *et al.* [213]. The energy of the neutral charge state is not well defined, as the defect will be auto ionised according to our calculations. The +1 charge state Li_i with one hydrogenic electron is -1.33 eV (BB1k) or -0.25 eV (B97-2) at octahedral site, which is lower than the neutral compact state.

At the octahedral site, in the +1 charge state, the Li ion moves towards three of the six neighbouring O atoms along the *c* axis, with the closest Li–O separation distance of 1.83 and the two other distances of 1.88 and 1.89 Å for both functionals, as shown in Figure 6.5(a)(b). For the neutral Li interstitial, the surrounding oxygens relax slightly outward (Figure 6.5 (c)(d)).

For the Li interstitial at the tetrahedral site, the surrounding O relax inward with the distances of 1.69, 1.90, 1.92 and 1.93 Å in the +1 charge state (Figure 6.5(e)(f)) for both functionals; Li is closer to the oxygen atom, repelling the Zn

atom. For the neutral state (Figure 6.5(g)(h)), the Li-O distance is slightly larger than that obtained for the +1 charge state.

charge	position		defect	funct	ional
state				BB1K	B97-2
0	octahedral	compact	Li [°] _i (oct)	0.67	0.65
		diffuse	$\text{Li}_{i}^{+}(\text{oct}) + e_{m^{*}}(\text{H})$	-1.33	-0.25
	tetrahedral	compact	Li [°] _i (tet)	1.50	1.50
		diffuse	$\text{Li}_{i}^{+}(\text{tet}) + e_{m^{*}}(\text{H})$	-0.54	0.44
+1	octahedral	compact	Li⁺ (oct)	-4.74	-3.65
	tetrahedral	compact	Li ⁺ _i (tet)	-3.94	-2.96

 Table 6.2 Calculated defect formation energies of Li_i in ZnO with the Fermi level at the VBM under Zn-rich conditions.



Figure 6.4 Formation energy of Li_i in ZnO as a function of Fermi level relative to the valence band maximum (VBM) under Zn-rich conditions.



Figure 6.5 Li interstitial in+1 and 0 charge states in ZnO.

6.2.3 Li_{Zn}-Li_i complexes and self-compensation

When point defects are combined to form defect pairs, the formation energy may differ from those of the single defects. Here, we also investigated two types of Li_{Zn}-Li_i complexes: one is the Li_{Zn} with the Li_i at the octahedral site (Li_{Zn}-Li_i(Cot)); the other has the Li_i at the tetrahedral site (Li_{Zn}-Li_i(Tet)).

The calculated formation energies of the complexes are shown in Table 6.3 and plotted in Figure 6.6. The formation energy of the Li_{Zn}-Li_{i(Oct)} in the +1 charge state under Zn-rich is -3.18 eV (BB1k), which is 0.90 eV lower that of Li_{Zn}-Li_{i(Tet)}. In the neutral charge state, the formation energy of Li_{Zn}-Li_{i(Oct)} is - 2.34 eV (BB1k), also 0.90 eV lower. For the B97-2 functional, the differences are 0.69 and 0.71 eV for the 0 and +1 charge states. The (+/0) transition levels of both Li_{Zn}-Li_{i(Oct)} and Li_{Zn}-Li_{i(Tet)} are found to lie at 0.84 eV from the valence band, which yields a deep donor level.

For the neutral Li_{Zn}-Li_{i(Oct)}, the Li-Li distance is 2.143 Å with Li_{Zn} moving towards one of the nonaxial O neighbour at a distance of 1.798 Å (Figure 6.7(a)). In the +1 charge state, the nonaxial O traps a hole with the O-Li_{Zn} distance increasing by 0.101 Å, and the Li-Li distance decreasing by 0.041 Å (Figure 6.7(b)). Similar structures are also observed for Li_{Zn}-Li_{i(Tet)}, with the Li-Li distance decreasing from 2.199 Å in the neutral charge state (Figure 6.7(c)) to 2.151 Å in the +1 charge state (Figure 6.7(d)).

Defect	Charge state	Formation energy		
		(eV)		
		B97-2	BB1k	
Li _{Zn} -Li _{i(Oct)}	0	-2.22	-2.34	
	+1	-2.68	-3.18	
Lizn-Li _{i(Tet)}	0	-1.53	-1.44	
	+1	-1.97	-2.28	

Table 6.3 Calculated defect formation energies of Li_{Zn} - Li_i in ZnO with the Fermi level at the VBM under Zn-rich conditions.

6.2 Li-related defects



Figure 6.6 Formation energy of Li_{Zn}-Li_i in ZnO as a function of Fermi level relative to the valence band maximum (VBM) under Zn-rich conditions.



Figure 6.7 Lizn-Li; in 0 and +1 charge states in ZnO using the BB1k density functional.

6.2.4 Li_{Zn}-V_o complexes

For the complexes of Li_{Zn} with V_o, in the +1 charge state, the nearest three Zn neighbours of the vacant O are relaxed outward by 0.28 Å, with the neighbouring Li_{Zn} relaxed outward by 0.34 Å as shown in Figure 6.8. The distances from Li to three nonaxial O are 1.834, 1.834 and 1.841 Å using the BB1k functional. For the -1 charge state, two electrons are trapped at the vacancy site; the three Zn neighbours are displaced inward by 0.37Å, with the Li_{Zn} relaxed only slightly inward.

The formation energies of Li_{Zn}-V_O complexes in the -1, 0 and +1 charge states are shown in Figure 6.9. The Li_{Zn}-V_O complex is stable in the +1 state with transition level ε (+/-) at 3.06 eV using PBE0. For BB1k, the transition is above the CBM. The complexes act as donors in ZnO.



Figure 6.8 Li_{Zn} -V₀ in +1 (left) and -1 (right) charge states in ZnO using the BB1k.



Figure 6.9 Formation energy of Li_{Zn} - V_0 in ZnO as a function of Fermi level relative to the valence band maximum (VBM) under Zn-rich conditions.

6.2.5 Formation energies

Based on above results, the formation energies of Lizn, Li, Lizn-Li, Lizn-Vo and Vo under Zn-rich conditions are summarised in Figure 6.10. We found that, the Lizn-Li_{i(Oct)} complex has the lowest formation energy for the Fermi level near the CBM. The Lizn-Li_{i(Tet)} complex has the next lowest formation energy, which is 0.24 eV (B97-2) or 1.29 eV (BB1k) lower than single Lizn for the Fermi level near the CBM. The oxygen vacancy has a relatively high formation energy for the Fermi level near the CBM. The CBM. The oxygen vacancy has a relatively high formation energy for the Fermi level near the CBM. The Li_{i(Oct)} (B97-2) or Lizn-Vo complex (BB1k) becomes more stable than the Lizn-Li_{i(Oct)} complexes for the Fermi level in the middle of the band. When the Fermi level is near the VBM, the native oxygen vacancy becomes the dominant defect type.



Figure 6.10 Formation energy of Li related defects in ZnO as a function of Fermi level relative to the valence band maximum (VBM).

6.3 H-related defects

6.3.1 H interstitial H_i

Hydrogen is one of the most common impurities in semiconductors. Hydrogen is ubiquitous and has a high diffusivity inside the semiconductor. H may act as a donor or acceptor depending on the Fermi level. However, van de Walle predicted that hydrogen is an important shallow donor in ZnO using LDA first-principles calculations. [13]

In addition to standard octahedral and tetrahedral interstitials, there are two possible positions for hydrogen bonding to the anion atom: the body centred (BC) site and the "antibonding" (AB) site ¹, with two orientations, along the *c* axis (II) and in the *ab* layer, nearly orthogonal to the *c* axis. (\perp) (as shown in Figure 6.11) – the nomenclature introduced by Van de Walle. [13]



Figure 6.11 Hydrogen interstitial sites in ZnO.

¹ The term "antibonding" refers here to the geometry where the interstitial atom is located on the continuation of the bond rather than at the bond centre.

The formation energies of H interstitial are determined by the following reaction:

$$\frac{1}{2}H_{2(g)} \to H_i^{q+} + qe^-.$$
(6.3)

The calculated formation energies of the H interstitial at the octahedral and tetrahedral sites are shown in Table 6.4. The H interstitial is stable in the neutral charge state with formation energies of 2.59 eV for H_{i-oct} and 3.20 eV for H_{i-tet} using BB1k. In the positive charge state, the octahedral interstitial relaxes into the AB₁ site (Figure 6.12 (b)), and the tetrahedral interstitial relaxed into the AB₁ site (Figure 6.12 (d)).

Table 6.4 Calculated defect formation energies of H_i at octahedral and tetrahedral sites in ZnO with the Fermi level at the VBM.

	Charge state	Formation energy (eV)				
Defect		B97-2	PBE0	BB1k		
Hi-oct	-1	5.67	5.64	6.36		
H _{i-oct}	0	2.81	2.44	2.59		
H _{i-oct}	+1	-2.29	-2.41	-3.10		
H _{i-tet}	-1	6.33	6.12	7.00		
Hi-tet	0	3.22	2.89	3.20		
H _{i-tet}	+1	-2.16	-2.49	-3.01		



Figure 6.12 H interstitial at octahedral and tetrahedral sites in charge state 0 (a)(c), +1 (b)(d) in ZnO. (BB1k structures)

The optical energy levels of H interstitials are given in Figure 6.13. The neutral H interstitials are stable at octahedral and tetrahedral sites, and positive charge states are stable at the body centred (BC) site and "antibonding" (AB) site.

The calculated formation energies of H interstitial in the +1 charge state are shown in Table 6.5. The BC_{II} configuration is most stable using B97-2, PBE0 or BB1K with lowest energies: -2.42 eV (B97-2), -2.73 eV (PBE0) and -3.15 eV (BB1k), which is in agreement with previous theoretical studies by Wardle *et al.* [218, 219] using Local-spin-density-functional (LSDF), Limpijumnong and Zhang [220] using LDA, and Bang and Chang [221] who also used LDA, but differs from Van de Walle [13] who reported that the BC₁ to be the most stable using LDA. Our result is, however, in agreement with some experimental results. Based on polarisation studies and first principle calculations, Lavrov *et al.* [222] proposed the interstitial H to be at the BC_{II} site with an IR peak at 3611 cm⁻¹. Seager and Myers [223] also observed a similar peak. Jokela and McCluskey *et al.* [224] discovered a different IR peak at 3326 cm⁻¹ of H which they attributed to the AB₁ site. The formation energies of H⁺ are low enough to allow for large solubility of hydrogen in *n*-type ZnO. So, the experimental situation with attribution of vibrational spectroscopic features is still confused.

	Formation energy (eV)					
Defect	B97-2	PBE0	BB1k	LDA [13]	LDA [220]	LSDF [219]
H _{i (BC∥)}	-2.42	-2.73	-3.15	-1.82	X+0	X+0
Hi (AB⊥)	-2.24	-2.56	-3.08	-1.78	X+0.14	X+0.2
Hi (ABII)	-2.19	-2.52	-3.02	-1.59	X+0.17	X+0.2
H _{i (BC⊥)}	-2.14	-2.45	-2.96	-1.84	X+0.15	X+0.2

Table 6.5 Calculated defect formation energies of H_i in +1 charge state in ZnO when the Fermi level at the VBM.



Figure 6.13 Optical energy levels of H_i in ZnO with respect to band edges, calculated using the BB1k, PBE0 and B97-2 density functional.
The O-H distances of the H interstitial in ZnO are summarised in Table 6.6. For the AB_{\perp} configuration, the O-H distance is 0.977 Å (PBE0, Figure 6.14 (a)) or 0.973 Å (BB1k, Figure 6.14 (b)), as the O atom moves outward from its lattice site, which results in the Zn-O distance being 20% longer than the equilibrium Zn-O distance. The O-H bond length is close to the length of an hydroxyl ion in NaOH which is 0.98 Å [225]. For the AB_I configuration, the O-H distance is 0.972 Å (PBE0, Figure 6.14 (c)) or 0.973 Å (BB1k, Figure 6.14 (d)). Four Zn neighbours of O are relaxed outward with the distance from the Zn atom along the caxis to the O atom being 13.4% longer than the equilibrium Zn-O distance. The Zn atom nearest to the H atom in the BC₁ configuration is pushed away from its original lattice site along the Zn-O bond. The H-O distance is 0.956 Å (PBE0, Figure 6.14 (e)) or 0.950 Å (BB1k, Figure 6.14 (f)) and the Zn-O becomes 2.945 Å (PBE0) or 2.944 Å (BB1k). For the BC_I configuration, the H-O distance is 0.956 Å (PBE0, Figure 6.14 (g)) or 0.950 Å (BB1k, Figure 6.14 (h)), the Zn atom also moves outward with the Zn-O distance at 3.045 Å (PBE0) or 3.042 Å (BB1k).

	O-H distance (Å)					
Defect	B97-2	PBE0	BB1k	LDA [13]	LDA [220]	
H _{i (BCII)}	0.957	0.962	0.959	0.99	0.986	
H _{i (AB⊥)}	0.973	0.977	0.973	1.01	1.003	
Hi (ABII)	0.972	0.973	0.972	1.01	1.003	
Hi (BC⊥)	0.953	0.956	0.950	0.99	0.982	

Table 6.6 Calculated O-H distance of H_i in +1 charge state in ZnO with the Fermi level at the VBM.



Figure 6.14 Hydrogen interstitials at +1 charge state in ZnO. ($AB_{\perp}(1^{st} \text{ row}), AB_{\parallel}(2^{nd} \text{ row}), BC_{\perp}(3^{rd} \text{ row})$ and $BC_{\parallel}(4^{th} \text{ row})$.

6.3.2 H substitutional H_o

The formation energies of H substitutional are determined by following reaction under O poor conditions:

$$\frac{1}{2}H_{2(g)} + Zn_{(s)} + O_0^0 \to H_0^{q+} + ZnO_{(s)} + qe^-, \qquad (6.4)$$

Here, we limit the investigation focussing on a single H substitution, but more H ions might be accommodated around the site.

The optical level energies of the H substitutional are shown in Figure 6.16. We find that the H substitutional is stable in the +1 charge state.

The calculated formation energies of the H substitutional are shown in Table 6.7 and plotted in Figure 6.15. We find that H₀⁺ is 0.86 eV (B97-2), 0.55 eV (PBE0) or 0.58 eV (BB1k) lower than H_i⁺ at BC_{II} site, which is different from the results of Janotti and Van de Walle [214] who reported that the formation energy of H₀⁺ is ~0.1 eV higher than the formation energy of H_i⁺ using LDA and LDA+*U*, and Oba *et al.* [66], who reported the formation at same level (~-2.2eV under O poor) using HSE. Our result is in good agreement with the Raman study of Koch *et al.* [226] who reported that H₀ is energetically favoured compared to H_{i(BC)}.

The +/0 transition level is 4.50 eV (B97-2) or 4.54 eV (PBE0) or 5.47 eV (BB1k) above VBM, while Oba *et al.* [66] reported the +/0 level near the conduction band. The Ho⁺ is stable in ZnO, and acts as a shallow donor, which agrees with previous experimental results by Lavrov [227] who identified Ho as a shallow donor by Raman scattering and IR absorption spectroscopy.

6.3 H-related defects

Charge state	Formation energy (eV)				
	B97-2	PBE0	BB1k		
-1	6.47	6.50	7.82		
0	1.22	1.25	1.75		
+1	-3.28	-3.28	-3.73		

Table 6.7 Calculated defect formation energies of H_0 in ZnO when the Fermi level is at the VBM under O-poor conditions.



Figure 6.15 Formation energy of H_0 in ZnO as a function of Fermi level relative to the valence band maximum (VBM).



Figure 6.16 Optical energy levels of H_0 in ZnO with respect to band edges, calculated using the BB1k density functional.

6.4 Lizn-Hi complexes

The formation energy of the Li_{Zn} -H_i complex is determined by the following reaction:

$$Li_{(s)} + Zn_{zn}^{\times} + \frac{1}{2}H_{2(g)} \rightarrow Li_{Zn}H_i + Zn_{(s)}.$$
 (6.5)

under Zn rich/ O poor conditions.

The binding energy is calculated from:

$$E^{b}(\text{Li}_{\text{Zn}} - \text{H}) = E^{f}(\text{Li}_{\text{Zn}}^{-}) + E^{f}(\text{H}_{\text{i}}^{+}) - E^{f}(\text{Li}_{\text{Zn}}\text{H}_{\text{i}}).$$
(6.6)

The local structures of Li substitutional – H interstitial complexes are shown in Figure 6.17. The calculated formation energies and binding energies of Li substitutional – H interstitial complexes are shown in Table 6.8 and Table 6.9. Here we concentrate on the complexes of Li_{Zn} with nearby H_i. As with H_i, the complex with the H interstitial occupying the BC_{II} site is stable using all three functionals with the lowest energies of -1.34 eV (B97-2), -1.15 eV (PBE0) and --1.10 eV (BB1k) under O poor condition, which is in agreement with previous theoretical studies by Lee and Chang [75] and Wardle *et al.* [213]. The binding energies are between 0.91-1.28 eV, which are within the range reported by Lee and Chang [75], indicating that H atoms tend to form neutral defect complexes with acceptors.

Based on the most stable H interstitial position, which is $H_{i(BCII)}$, we investigated the different charge states:-1, 0 and +1, using PBE0. The formation energies are shown in Table 6.10 and plotted in Figure 6.17. From the results, we found that, the $H_{i(BCII)}$, is stable in the neutral charge state with the Fermi level across most of the gap and the (+1/0) transition level at 0.35 eV above the VBM.



Figure 6.17 Li_{Zn} - H_i complexes in ZnO.

6.4 LiZn-Hi complexes

Defect	Formation energy (eV)						
	B97-2 PBE0 BB1k LDA [75]						
Lizn-Hi (BCII)	-1.34	-1.15	-1.10	-2.47			
Lizn-Hi (AB⊥)	-1.22	-1.02	-0.93	-2.17			
Lizn-Hi (ABII)	-1.23	-1.07	-1.02	-1.96			
Li _{Zn} -H _{i (BC⊥)}	-1.20	-1.00	-0.92	-2.36			

 Table 6.8 Calculated defect formation energies of neutral Lizn-Hi in ZnO under Zn-rich conditions.

Table 6.9 Calculated binding energies of neutral Li_{Zn} - H_i in ZnO.

Defect	Binding energy (eV)				
	B97-2	PBE0	BB1k	LDA [75]	
Li _{Zn} -H _{i (BCII)}	1.07	0.91	1.23	1.22	
Li _{Zn} -H _{i (AB⊥)}	1.12	0.96	1.13	0.71	
Lizn-Hi (ABII)	1.19	1.05	1.28	0.92	
Li _{Zn} -H _{i (BC⊥)}	1.20	1.05	1.24	1.11	

Table 6.10 Calculated defect formation energies of Li_{Zn} - $H_{i(BCII)}$ in ZnO with the Fermi level at the VBM under Zn-rich conditions.

Charge state	Formation energy (eV)
	PBE0
-1	3.90
0	-1.15
+1	-1.50



Figure 6.18 Formation energy of Li_{Zn} - $H_{i (BCII)}$ in ZnO as a function of the Fermi level relative to the valence band maximum (VBM) using the PBE0 functional under Zn-rich conditions.

There are other possible complex configurations, including the complex with the H_i further from the Li_{Zn}. To investigate the influence of the H_i position on the defect properties, we present two examples for comparison. Figure 6.19, (a) shows the Li_{Zn}-H_{i(AB_⊥)} configuration with H_i next to Li_{Zn}, while (b) gives the Li_{Zn}-H_{i(AB_⊥)-2} configuration with H_i and Li_{Zn} bonded to the same oxygen but in an opposite direction.

The defect formation energies are calculated using PBE0 as shown in Table 6.11. We found that for both Li_{Zn} - $H_{i(AB \perp)}$ and Li_{Zn} - $H_{i(ABI)}$ complexes, the complexes with H_i further from the Li_{Zn} are less stable than the complexes with H_i adjacent to the Li_{Zn} , with formation energies 0.19-0.28 eV higher. Therefore, the Li_{Zn} - H_i tend to form the complexes with the defects adjacent to each other.

Table 6.11 Calculated defect formation energies of Li_{Zn} - $H_{i(AB_{\perp})}$ and Li_{Zn} - $H_{i(AB_{\parallel})}$ in ZnO with theFermi level at the VBM under Zn-rich conditions.

Defect	Formation energy (eV)
	PBE0
$Li_{Zn}\text{-}H_{i(AB\perp)}$	-1.02
$Li_{Zn}\text{-}H_{i(AB\perp)\text{-}2}$	-0.74
Lizn-H _{i(ABII)}	-1.07
Lizn-Hi(ABII)-2	-0.88



Figure 6.19 Li_{Zn} - H_i complex in ZnO.

6.5 Summary and Conclusion

The defect properties of Li or H doped ZnO with various defects have been studied by calculating the structures and defect formation energies using QM/MM approach, using three density functionals: B97-2, PBE0 or BB1K.

The results from the formation energy calculations show that, Li_{Zn} acts as a deep acceptor in ZnO. Li interstitial at the octahedral site is more stable than at the tetrahedral site. The Li_{Zn}-Li_{i(Oct)} complex has the lowest formation energy for the Fermi level near the CBM in O-poor conditions. The Li_{i(Oct)} (B97-2) or Li_{Zn}-V_O complex (BB1k) becomes more stable than the Li_{Zn}-Li_{i(Oct)} complex for the Fermi level near the VBM.

We identified that the H interstitial is most stable in BC_I configuration in positive charge state with the energies of other configurations in the order BC_{\perp} < AB_I <

 AB_{\perp} . H_i is stable in ZnO and acts as a shallow donor.

The H_o also acts as a shallow donor in the positive charge state in ZnO. We also found that, the formation energy of H_o⁺ is 0.55-0.86 eV lower than that of H_i⁺ at the BC_I site, indicating that H_o⁺ is more stable then H_i⁺.

For the complexes of Li_{Zn} with H_i , the most stable configurations are also the complexes with the H_i at the BC_{II} site next to the Li_{Zn} . The complexes act as shallow donors in ZnO.

Chapter 7

Intrinsic point defects in In₂O₃

7.1 Introduction

As discussed in Chapter 2, In_2O_3 is an intrinsic *n*-type semiconductor which is one of the most frequently used TCO materials, and a large number of experimental and theoretical studies have been carried out to date on the material. However, the cause of the unintentional *n*-type conductivity in In_2O_3 is still a subject of debate.

In Chapter 4, we investigated the defect properties of In₂O₃ using an interatomic potential method, which allowed us to gain useful information about defect energies and structures. However, atomistic simulations based on interatomic potentials neglect the quantum aspects of the nuclear and electronic degrees of freedom, so that the electron structures and states cannot be calculated directly. Quantum Mechanical methods must be used to construct realistic models of the electronic structure of many-body systems. This Chapter therefore applies QM methods to obtain detailed information about the electronic structure of the intrinsic defects in various charge states; we also provide further analysis of their formation energies and their dependence on the position of the Fermi level which is beyond the scope of atomistic methods

The commonly used QM approach to modelling defect formation in In_2O_3 is density functional theory (DFT) employing a plane-wave basis set under periodic boundary conditions, which, unfortunately, as we have noted, can suffer from finite-size effects. Moreover, as discussed earlier, the supercell approximation introduces artificial interactions between charged defects, which need to be corrected for, but the optimum approach is still a matter of debate [228].

In this Chapter, the study of intrinsic point defects in In₂O₃ is presented using the QM/MM approach. The formation energies, transition levels and structures of all possible intrinsic point defects are investigated including oxygen vacancy (V₀), indium vacancy (V_{in}), indium interstitial (In_i) and oxygen interstitial (O_i).

7.2 Calculation Settings

The hybrid QM/MM embedded cluster technique (Chapter 3.2.5) is employed to calculate bulk and defect energies in In₂O₃. In our QM/MM model, the inner cluster of 97 atoms of bixbyite In₂O₃ containing the central defect and its surrounding atoms is treated with a QM method. We have employed two exchange and correlation functionals, the PBE0 functional [118], which is frequently used in plane-wave basis calculations including 25% exact exchange; and B97-2 functional [119], which has been fitted to a broad range of thermochemical date with 21% exact exchange. Future studies will amply BB1k functionals on the most significant configurations identified in this work. The outer region which contains 9704 atoms is treated with the MM method using interatomic potentials [120]. Between the QM and MM regions, a specially designed local ECP (section 3.3.4) giving in Table 3.1 is placed on the cation sites within a range of 5 Å from the edge of the QM region.

7.3 Ionization potentials

The calculated ionization potentials (IPs) as the energy difference between the positively charged cluster and the neutral one are given in Table 7.1.

As discussed in Chapter 5.3, the bulk ionization potential can be higher or lower than the surface IP but would be expected to be close for well prepared / equilibrated experimental samples, subject to the surface band bending. Therefore, the agreement between our calculations and others in the literature and experiment is good. The large calculated values of the IP positions the VB deep below the vacuum level.

Therefore, as with In_2O_3 hole formation has a high energy, while the formation energy of positively charged defect (e.g., oxygen vacancies) will be low when the Fermi level is close to the VBM, which explains the observed difficulty in *p*type doping In_2O_3 .

Functional	IPs
PBE0	7.59
B97-2	7.30
Previous calculations	6.8-7.9 [42, 173, 174, 229]
Experiment	7.0-7.7 [150, 151, 178]

Table 7.1 Calculated ionization potentials (eV) of In_2O_3 .

7.4 Compact defect states and structures

7.4.1 O vacancy V₀

The O ions in In_2O_3 are surrounded by four In ions with the In-O distances of 2.09, 2.10, 2.12, and 2.20 Å. For the neutral charge state, two electrons are trapped at the vacancy site, two of the four nearest Zn neighbours are relaxed inward by 0.12 and 0.01Å but the two others are displaced outward by 0.10 Å as shown in Figure 7.2 (a).

In the +2 charge state, after removal of two electrons to form the vacancy, the four In atoms strongly relax outward by 0.17, 0.12, 0.17 and 0.25 Å as shown in Figure 7.2 (c), which is similar with the case of V₀ in ZnO (section 5.4.2).



Figure 7.1 Optical energy levels of V_0 in In_2O_3 with respect to band edges, calculated using the PBE0 and B97-2 density functional.



Figure 7.2 O vacancy in In_2O_3 by PBE0.

7.3.2 In vacancy V_{in}

There are two inequivalent indium sites in the In_2O_3 structure: the 8*b* site and the 24*d* site.

For both inequivalent In sites, a missing In^{3+} ion leaves the -3 state of the indium vacancy with no electrons remaining in the vacant site as the Madelung potential destabilises the electron states of cation vacancies. In the -3 state, the three electrons contributed by the original In ion at the vacant site occupy the three nearest neighbour O ions. The six nearest neighbour O^{2-} ions of the original vacant In ion relax outward as shown in Figure 7.4 (e) (f).

The electron rich V_{In}^{3-} state can lose electrons from the surrounding O ions. In the -2 state, one of the three neighbour O ions binds a hole, forming a spin doublet as shown in Figure 7.4 (d) (i). In the -1 state, two of the O ions each bind a hole, forming a spin triplet (Figure 7.4 (c) and (h)), while in the neutral state, either all three O ions bind a hole each stabilising as a spin quadruplet (Figure 7.4 (b) (g)), or two O ions bind three holes resulting in a spin doublet (Figure 7.4 (a) (f)).

All the charge states -3, -2, -1 and 0 introduce donor energy levels in the bandgap, as shown in Figure 7.3.

7.4 Compact defect states and structures



Figure 7.3 Optical energy levels of V_{In} in In₂O₃ with respect to band edges, calculated using the PBE0 and B97-2 density functional.



Figure 7.4 In vacancy in In₂O₃ at 8b site (left) and 24d site(right) by PBE0. The spin densities of the 0, -1, and -2 state are indicated by isosurfaces 0.1, 0.05, 0.025 au highlighted in yellow.

7.3.3 O interstitial O_i

As with In_i , we only investigated the O interstitial at the 16*c* site, shown previously to be the most stable.

A neutral oxygen interstitial in the triplet state at the 16*c* site remains at the site. After excitation to the singlet state, the atom relaxes into the split interstitial position. The ground state electronic configuration of the neutral split oxygen interstitial is a singlet, while the neutral 16*c* oxygen interstitial is a triplet. The formation energy of the neutral split oxygen interstitial under O-rich conditions is 1.79 (B97-2) or 1.47 eV (PBE0), while that of the neutral 16*c* oxygen interstitial is 3.85 (B97-2) or 3.86 eV (PBE0).

The O interstitial in charge states -2, -1 and 0 introduce donor energy levels in the bandgap, calculated by B97-2 and PBE0, as shown in Figure 7.5.

In the O split interstitial configuration (Figure 7.7), the calculated O-O distances are 1.489 Å for both functionals, suggesting the formation of an O-O chemical bond.



Figure 7.5 Optical energy levels of O_i in In_2O_3 with respect to band edges, calculated using the PBE0 and B97-2 density functional.



Figure 7.6 Oxygen interstitial at 16c site in 0 (a), -1 (b) and -2 (c) charge states in In_2O_3 by PBE0. The spin densities of the 0 and -1 state are indicated by isosurfaces 0.1, 0.05, 0.025 au highlighted in yellow.



Figure 7.7 Split oxygen interstitial in 0 charge state in In₂O₃by PBE0.

7.3.4 In interstitial In_i

In In_2O_3 , there are at least three possible interstitial sites, 8*a*, 16*c* or 24*d*. According to the results in Chapter 4.5, both cation and anion interstitials have the lowest defect energies at the 16*c* site, which agrees with previous DFT calculations [230]. Hence, here, we only concentrate on the In interstitial at the 16*c* site.

The local highest occupied state, +3 state is pushed below the VBM by 2.46-2.47 eV (Figure 7.8) which can attract electrons. However, the electrons trapped on the In_i ion are delocalised. The In_i is close to three nearest O at a distance of 2.07 Å, and three other O of 2.18 Å (Figure 7.9 (d)). Trapping of electrons results in the neighbour O ions relaxing outward. In the neutral state, the In_i -O bond lengths have two groups of three at 2.10 Å and 2.64 Å (Figure 7.9 (a)).



Figure 7.8 Optical energy levels of In_i in In_2O_3 with respect to band edges, calculated using the PBE0 and B97-2 density functional.



Figure 7.9 In interstitial at 16c site in 0 (a), +1 (b), +2 (c) and +3 (d) charge states in In₂O₃ by PBE0. The spin densities of the 0 and +1 states are indicated by isosurfaces 0.1, 0.05, 0.025 au highlighted in yellow, +2 state is indicated by isosurfaces 0.005, 0.0025, 0.002 au highlighted in yellow.

7.5 Diffuse defect states

To calculate the binding energies of electrons or holes using equation (3.30) - (3.32) in section 3.4.1, we take computed value of ε (9.77) for ln₂O₃ from our interatomic forcefields, and experimental value of $m^*:m_e^* = 0.22m_e$ [231] for electrons $m_h^* = 0.6m_e$ [232-234] for holes. The binding energy for one or two diffuse electrons (to CBM) or holes (to VBM) for ln₂O₃ are summarised in Table 7.2.

electrons	Binding energy (eV)	holes	Binding energy (eV)
e _{m*} (H) for +1	-0.037	h _{m*} +(H) for -1	-0.100
e _{m*} (H) for +2	-0.146	h _{m*} +(H) for -2	-0.399
2e [*] _{m*} (He) for +2	-0.212	2h ⁺ _{m*} (He) for -2	-0.578
2e [*] _m (Hydride) for +1	-0.039	2 h _{m⁺} (Hydride) for -1	-0.105

Table 7.2 The binding energies (in eV) of the diffuse electrons and holes in In_2O_3 .

The calculated energies of compact and diffuse defect states (see section 3.4.1) for each defect and density functional are given in Table 7.3 to Table 7.6. The energies (in eV) are given for the Fermi energy at the CBM with the electron in the CB and the hole in the VB.

charge state		defect	func	tional
			B97-2	PBE0
0	compact	In ^o i	5.90	5.27
	diffuse	In ⁺ _i + e ⁻ _{m⁺} (H)	3.06	2.37
		In ²⁺ _i + 2e ⁻ _{m*} (He)	1.27	0.69
1+	compact	In ⁺	3.10	2.40
	diffuse	In ²⁺ _i + e ⁻ _{m*} (H)	1.34	0.76
2+	compact	In ²⁺	1.48	0.90
	diffuse	$\ln_{i}^{+} + h_{m^{\star}}^{+}(H)$	5.70	5.00

Table 7.3 The energies (in eV) of the compact and diffuse state of In_i in In_2O_3 .

7.5 Diffuse defect states

charge state		defect	func	functional	
			B97-2	PBE0	
0	compact	V _o	0.87	0.95	
	diffuse	$V_{0}^{+} + e_{m}^{-}(H)$	0.41	0.36	
		V ₀ ²⁺ + 2e _{m*} (He)	-0.27	0.01	
1+	compact	V _o ⁺	0.44	0.39	
	diffuse	$V_{O}^{2+} + e_{m^{*}}(H)$	-0.20	0.07	
2+	compact	V ₀ ²⁺	-0.05	3.04	
	diffuse	$V_{0}^{+} + h_{m^{+}}^{+}(H)$	0.21	2.99	

Table 7. 4 The Energies (in eV) of the compact and diffuse state of V_0 in In_2O_3 .

Table 7.5 The Energies (in eV) of the compact and diffuse state of O_i in In_2O_3 .

charge state		defect	functional	
			B97-2	PBE0
0	compact	O ⁰ _i	7.10	7.11
	diffuse	$O_i^+ + h_{m^*}^+(H)$	9.13	9.04
		O ²⁻ _i +2 h ⁺ _{m*} (He)	11.62	11.41
1-	compact	O _i	6.53	6.44
	diffuse	$O_{i}^{2-} + h_{m^{*}}^{+}(H)$	9.10	8.89
2-	compact	0 ²⁻ _i	6.80	6.59
	diffuse	O _i (+ e _{m*} (H)	6.49	6.40

7.5 Diffuse defect states

defect position	charge state		defect	funct	ional
				B97-2	PBE0
V _{In-8b}	0	compact	V _{In}	11.37	12.40
		diffuse	V _{In} +h ⁺ _{m*} (H)	13.18	14.31
			V ²⁻ _{In} +2h ²⁻ _i (He)	15.18	16.45
	1-	compact	Vin	10.58	11.71
			$V_{ln}^{2-} + h_{i}^{2-}(H)$	12.66	13.93
	2-	compact	V ²⁻ In	10.35	11.63
		diffuse	V _{in} +e _{m⁺} (H)	10.54	11.68
	3-	compact	V ³⁻ _{In}	10.46	11.54
		diffuse	V ²⁻ _{In} + e _{In} (H)	10.21	11.48
			V _{In} +2e _{In} (Hydride)	10.54	11.68
V _{In-24d}	0	compact	V _{In}	11.02	12.06
		diffuse	$V_{in}^{-}+h_{m^{*}}^{+}(H)$	13.10	14.29
			$V_{ln}^{2-}+2h_{i}^{2-}(He)$	15.28	16.46
	1-	compact	Vin	10.50	11.68
			$V_{ln}^{2-} + h_{i}^{2-}(H)$	12.76	13.94
	2-	compact	V ²⁻ In	10.46	11.64
		diffuse	V _{in} +e _{m⁺} (H)	10.47	11.65
	3-	compact	V ³⁻ _{In}	10.38	11.66
		diffuse	V ²⁻ _{In} + e ⁻ _{In} (H)	10.32	11.49
			V _{In} +2e _{In} (Hydride)	10.46	11.65

Table 7.6 The Energies (in eV) of the compact and diffuse state of V_{In} in In_2O_3 .

7.6 Formation energies

The formation energies of defects are determined by following reactions:

$$\ln_{\ln}^{\times} \to V_{\ln}^{q^-} + \ln_{(s)} + qh^+$$
, (7.1)

$$\frac{1}{3} \ln_2 O_{3(s)} \to O_i^{q-} + \frac{2}{3} \ln_{(s)} + q h^+ , \qquad (7.2)$$

$$\ln_{(s)} \to \ln_{i}^{q+} + qe^{-}$$
, (7.3)

$$0_0^0 + \frac{2}{3} \ln_{(s)} \to V_0^{q+} + \frac{1}{3} \ln_2 0_{3(s)} + q e^-, \qquad (7.4)$$

for indium rich/oxygen poor conditions, and

$$\ln_{\ln}^{\times} + \frac{3}{4}O_{2(g)} \to V_{\ln}^{q-} + \frac{1}{2}\ln_2 O_{3(s)} + qh^+ , \qquad (7.5)$$

$$\frac{1}{2}O_{2(g)} \to O_i^{q-} + qh^+, \qquad (7.6)$$

$$\frac{1}{2} \ln_2 O_{3(s)} \to \ln_i^{q+} + \frac{3}{4} O_{2(g)} + q e^- , \qquad (7.7)$$

$$0_0^0 \to V_0^{q+} + \frac{1}{2} O_{2(g)} + q e^-,$$
 (7.8)

for indium poor/oxygen rich conditions. The chemical potentials of O₂ molecular and single In atoms are calculated using GAMESS-UK with the corresponding basis set and density functional: the standard state energy of In₂O₃ is derived from the experimental heat of formation [49].

Figure 7.10 shows the formation energies as a function of the Fermi level for all above point defects in In_2O_3 for O-rich and O-poor conditions.



Figure 7.10 Formation energy of point defects in In_2O_3 as a function of Fermi level relative to the valence band maximum (VBM) under In-rich and O-rich conditions.

The oxygen vacancy V₀ is stable in the +2 charge state for Fermi level positions across the gap. The V₀ is a shallow donor with the (+2/+) and (+/0) transition levels above the CBM. The formation energy of V_0^{2+} near VBM is negative, indicating a spontaneous formation, which will suppress positive free charge carriers, or holes.

The formation energy of the neutral oxygen vacancy is 4.12 eV (B97-2) or 4.20 eV (PBE0) in O-rich conditions which agrees well with Liu *et al.* [235] who reported 4.11 eV using the GGA+U and with those of Agoston *et al.* [153] using HSE06 functional, but is ~1.5 eV lower than the corrLDA+U results by Reunchan *et al.* [27]

The formation energy of neutral V_{In} at the 8*b* site is 0.35 eV (B97-2) or 0.34 eV (PBE0) higher than that of the vacancy at the 24*d* site. This is lower than the

1eV reported by Chatratin *et al.* [236] using HSE with 28% HF mixing parameter, but higher than the ~0.1 eV calculated by Varley *et al.* [85] by HSE06 with 32% HF mixing parameter. For the 3- charge state, the difference is only 0.1 eV for both functionals, which is similar to the HSE results.

We find that high-spin is more favourable than the low-spin state for the charge neutral state V_{In} at 24*d*. However, it is the opposite for neutral V_{In} at the 8*b* site. The transition levels of (0/-1), (-1/-2) and (-2/-3) are 1.91 eV, 2.48 eV, 2.81 eV (B97-2) and 2.02 eV, 2.61 eV, 2.62 eV (PBE0) for V_{In} at 8*b*, and 2.19 eV, 2.62 eV, 2.66 eV, 2.66 eV (B97-2) and 2.33 eV, 2.66 eV, 2.72 eV (PBE0) for V_{In} at 24*b*, above the VBM. The formation energies of V_{In} are very high for the Fermi level in the gap, indicating that In vacancies are unlikely to be present.

In_i is mostly stable in the +3 charge states for Fermi level position across the gap, with (+3/+2) transition level over CBM. In O-poor conditions, In_i acts as *n*-type donor as it has low formation energy and positive charge state for the Fermi level close to the CBM. In O-rich conditions, its energy increases. When the Fermi level is close to the CBM, compensation by O_i defects occurs, as it has the lowest energy.

The O_i at 16*c* acts as a very deep acceptor, with transition level ε (0/-) at 2.13 eV (B97-2) or 2.03 eV (PBE0) above the VBM. The transition level ε (-/2-) is above the CBM. In the split interstitial configuration, the O_i is electrically neutral for the Fermi level within the gap. The formation energy of the neutral split oxygen interstitial under O-rich is 2.06 (B97-2) or 2.49 eV (PBE0) is lower than that of the neutral 16*c* oxygen interstitial.

7.7 Ionization energies as defect (transition) levels

The calculated ionization energies (see section 3.4.3) for the full range of point defects and charge states in In_2O_3 are summarised in Table 7.7.

There are numerous studies on the common luminescence bands observed in In_2O_3 including violet to green and orange to red bands. The source of violet to green in In_2O_3 is mainly reported as due to oxygen vacancies. [233, 237-239]

The origin of the orange to red luminescence bands has been controversial. Mazzera *et al.* [237] observed a PL emission at ~630 mm (1.97 eV) in the \ln_2O_3 nanowires. They concluded that this orange emission arises from the contribution of oxygen vacancies and assigned it to the intrinsic defects of interstitial oxygen, indium vacancy and anti-site oxygen. In contrast, Gao and Wang [240] proposed that the 620 nm PL emission in the \ln_2O_3 nanobelts results from the recombination of a photoexcited hole with an electron occupied by the oxygen vacancy. From our calculations, we found the emission peak for capture of a hole by the +1 charge state V_0 is 2.14 eV (B97-2), by the +2 charge state \ln_i at octahedral site is 2.12 eV (B97-2), which might be the source of the orange emissions. We noted here that both PBE0 and B97-2 cannot reproduce good asymptotic behaviour of the Kohn-Sham potential. A more accurate functional such as BB1k is needed to reduce the one-electron self-interaction error in the traditional DFT formulations.

7.7 Ionization energies as defect (transition) levels

Summary of calculated ionisation energies										
Defect	B97-2					PBE0				
states	Epl	Eab	ZPL	Erel	E _{rel} *	Epl	Eab	ZPL	Erel	E _{rel} *
Vo										
V ₀ (+1 +2)e	-1.22	3.32	-0.50	0.73	3.91	-1.25	3.32	-0.18	1.07	3.50
Vo (0 +1)e	-0.95	0.56	-0.43	0.53	0.99	-1.05	0.22	-0.56	0.50	0.78
V ₀ (+2 +1)h	-0.62	3.92	3.20	3.81	0.73	-0.62	3.95	2.88	3.50	1.07
Vo (+1 0)h	2.14	3.65	3.13	0.99	0.53	2.48	1.05	3.26	0.78	0.50
V _{In} 8b										
V _{In} (-3 -2)e	-1.67	1.65	-0.11	1.56	1.76	-1.86	1.64	0.08	1.94	1.56
V _{In} (-2 -1)e	-0.81	1.42	0.22	1.03	1.20	-1.08	1.43	0.09	1.17	1.35
V _{In} (-1 0)e	0.08	1.58	0.79	0.71	0.80	-0.14	1.60	0.68	0.83	0.92
V _{In} (-2 -3)h	1.05	4.37	2.81	1.76	1.56	1.06	4.56	2.62	1.56	1.94
V _{In} (-1 -2)h	1.28	3.51	2.48	1.20	1.03	1.27	3.78	2.61	1.35	1.17
V _{In} (0 -1)h	1.12	2.62	1.91	0.80	0.71	1.10	2.84	2.02	0.92	0.83
V _{In} 24d										
V _{In} (-3 -2)e	-1.32	1.73	0.08	1.40	1.65	-1.55	1.78	-0.02	1.54	1.80
V _{In} (-2 -1)e	-0.64	1.51	0.04	0.68	1.47	-0.82	1.47	0.04	0.86	1.43
V _{In} (-1 0)e	0.18	1.73	0.51	0.33	1.22	-0.04	1.70	0.37	0.41	1.33
V _{In} (-2 -3)h	0.97	4.02	2.62	1.65	1.40	0.92	4.25	2.72	1.80	1.54
V _{In} (-1 -2)h	1.19	3.34	2.66	1.47	0.68	1.23	3.52	2.66	1.43	0.86
V _{In} (0 -1)h	0.97	2.52	2.19	1.22	0.33	1.00	2.74	2.33	1.33	0.41
Oi 16c										
O _i (-2 -1)e	-1.70	1.18	-0.27	1.43	1.45	-1.59	1.10	-0.15	1.45	1.25
Oi (-1 0)e	-0.21	1.64	0.57	0.78	1.07	-0.24	1.56	0.67	0.91	0.89
O _i (-1 -2)h	1.52	4.40	2.97	1.45	1.43	1.60	4.29	2.85	1.25	1.45
O _i (0 -1)h	1.06	2.91	2.13	1.07	0.78	1.14	2.94	2.03	0.89	0.91
In _i 16c										
In _i (+2 +3)e	-1.90	0.58	-0.31	1.58	0.90	-2.01	0.15	-1.07	0.94	1.23
In _i (+1 +2)e	-2.49	-0.72	-1.62	0.88	0.90	-2.84	-0.87	-1.50	1.34	0.63
In _i (0 +1)e	-3.08	-2.23	-2.80	0.28	0.57	-3.17	-2.34	-2.86	0.31	0.52
ln _i (+3 +2)h	2.12	4.60	3.01	0.90	1.58	2.55	4.71	3.77	1.23	0.94
ln _i (+2 +1)h	3.42	5.19	4.32	0.90	0.88	3.57	5.54	4.20	0.63	1.34
In _i (+1 0)h	4.93	5.78	5.50	0.57	0.28	5.04	5.87	5.56	0.52	0.31

Table 7.7 Summary of calculated ionization energies for the full range of point defects and charge states in In_2O_3

7.8 Summary and Conclusion

The structure, defect states, ionization potentials and defect formation energies of intrinsic point defects including oxygen vacancy, indium vacancy of 8*b* and 24*d* site, indium interstitial at 16*c* site and oxygen interstitial at 16*c* site in In_2O_3 have been investigated using the QM/MM approach with two functionals, B97-2 and PBE0.

The ionization potentials calculated using both B97-2 and PBE0 are in good agreement with earlier studies. Compared to the hole carriers, the electron carriers will remain stable as the valence band is deep.

We found that oxygen vacancies are shallow donors and indium vacancies at both 8*b* and 24*d* site are deep acceptors, with formation energy relatively high for Fermi level within the gap even under O-rich conditions. The oxygen interstitials at the 16*c* site are also deep acceptors, while the oxygen split interstitials are electrically neutral for the Fermi level within the gap. In interstitials at 16*c* are mostly stable in the +3 charge states for the Fermi level position across the gap.

In Chapter 4.6, we have reported the oxygen vacancy defect formation energies determined using interatomic potential methods. Here, we calculated the defect formation energies of four intrinsic point defects in In₂O₃ using interatomic potential methods. By comparing the IP results to the PBE0 results obtained using the QM/MM approach, we concluded that the IP values are underestimated; the QM/MM approach give results that are more accurate than those obtained using classical models.

Defect	O rich		O poor			
	QM/MM(PBE0)	IP	QM/MM(PBE0)	IP		
Vo ²⁺	-1.94	2.76	-5.19	-0.49		
V _{In} ³⁻ (8b)	14.77	23.45	19.64	28.32		
V _{In} ³⁻ (24d)	14.88	23.93	19.76	28.81		
Oi ²⁻	8.74	16.19	11.99	12.94		
Ini ³⁺	-3.39	-4.33	-8.27	0.54		

Table 7.8 Defect formation energies of four intrinsic point defects in In_2O_3 using IP and QM/MM methods.

7.8 Summary and Conclusion

In this Chapter, we have presented the investigation on the intrinsic point defects in In_2O_3 have using B97-2 and PBE0 functionals. However, as discussed in Chapter 5 and 6, the BB1k functional is expected to provide a better account of electron localisation and more accurate ionisation energies. The calculations in this chapter therefore provide a preliminary study on which future work using the BB1k functional will build.

Solid Solution of In₂O₃ and SnO₂

8.1 Introduction

As discussed earlier, solid solutions, in which SnO₂ is doped into In_2O_3 at lower concentrations are denoted as indium-tin oxide (ITO) and are efficient transparent conducting oxides. Nadaud *et al.* [241] studied the structure of ITO solid solutions, finding that the solubility of tin in indium oxide in ambient conditions is ~6%, and that the lattice parameter and oxygen/metal ratio increase with the tin doping concentration. Yamada *et al.* [242] investigated the doping mechanism of ITO prepared by the solid-state reaction method and explained that the repulsive force among tetravalent Sn with a higher effective charge than that of In^{3+} results in an increase in lattice constant. Gao *et al.* [243] achieved up to 6.4 at.% Sn doping concentrations using the physical vapor transport method.

At greater concentrations of Sn, there is a switch from electronic to ionic mechanism of maintaining charge neutrality, which we intend to explore. Moreover, there is at least one partially ordered intermediate phase and there could be more unknown phases which would be of general interest in crystallography and mineralogy. Heward and Swenson [244] determined the $In_2O_3 - SnO_2$ phase diagram in the region of 1000-1650°C using an electron probe microanalyzer (EPMA) and x-ray diffraction (XRD) analysis. The phase diagram (Fig.1 in ref [244]) is given in Figure 8.1. SnO_2 was found to have a maximum solubility of 13.1 mol% in In_2O_3 at 1650 °C. Two intermediate phases, $In_4Sn_3O_{12}$ and In_2SnO_5 , were found to exist over the studied temperature range.

In this Chapter, we present a preliminary modelling study of the solid solutions of In_2O_3 and SnO_2 using the IP from Chapter 4.3. The average properties of systems of different compositions have been calculated.



Figure 8.1 Phase diagram of the In₂O₃ - SnO₂ system. The solid triangles represent bulk compositions of samples used to obtain compositional data. [244]

8.2 Structure Generation

To simulate solid solutions of In_2O_3 and SnO_2 in more realistic system sizes, supercells are used. In this study, both a $1\times1\times1$ unit cell and $2\times2\times2$ supercells of In_2O_3 have been firstly used. On analysing the results, we found that a supercell into which both In_2O_3 and SnO_2 crystal structures can fit is needed to span the full stoichiometric range of the solid solution $In_{2-x}Sn_xO_{3+2x}$. Therefore, we additionally created an ideal supercell of SnO_2 that can fit in both rutile and bixbyite structures.

8.2.1 Supercell of bixbyite

For each two substitutional tin cations doped onto indium ion lattice sites in the $2\times2\times2$ supercells of In₂O₃, a charge compensating oxygen interstitial needs to be introduced. As one In₂O₃ unit cell of 80 atoms contains 32 cations and 16 oxygen interstitial sites. there are 128 oxygen interstitial sites and 256 cation sites that can be replaced in a $2\times2\times2$ supercell.

The number of possible structures for every doping concentration that contains different defect clusters (two substitutional tin ions and one interstitial oxygen ion) is

$$N = \frac{N_{all}!}{(N_{all} - N_{Sn})! N_{Sn}!} \times \frac{M_{all}!}{(M - M_O)! M_O!},$$
(8.1)

where *N* is the number of possible structures, N_{all} and M_{all} are the total numbers of cation and anion sites, N_{Sn} and M_o are the number of Sn and O dopants.

For the supercell that contains only one defect cluster, the number of structures is 4,177,920 without taking into account symmetry. Introducing more defect clusters will result in a huge number of possible structures, which makes exhaustive simulations impossible. For example, the number of possible structures increases to 1.26×10^{17} after introducing three defect clusters into the $2 \times 2 \times 2$ supercell of \ln_2O_3 . However, since the end-member system is symmetric, most structures are symmetrically equivalent.

In the KLMC approach, discussed in chapter 3.5.3, an unbiased Monte Carlo method is applied to obtain random sampling results of SnO_2 doping into In_2O_3 supercells. KLMC restricts anions from swapping with cations. All cations including original indium ions and substitutional tin ions are allowed to randomly occupy the lattice cation sites. There are two different ways to set up the anion sites: one allows both lattice and interstitial O anions to occupy both lattice anion positions and the interstitial anion sites (R1), the other only allowed the O dopants to occupy the interstitial anion sites (R2).

We firstly generated ~1000 unique structures for every tin dopant concentration in a $1\times1\times1$ unit cell of In_2O_3 and performed energy optimisations using potentials listed in Table 4.1 which are designed to reproduce good lattice properties. The initial lattice parameters used are the parameters of In_2O_3 . To provide relevant dopant concentrations in more realistic system sizes, we then further investigated the $2\times2\times2$ supercells. We randomly generated ~10,000 unique structures for ~60 out of 128 possible different tin dopant concentrations in the $2\times2\times2$ supercells of In_2O_3 .

8.2.2 Supercell of rutile

Under ambient conditions, SnO_2 adopts the rutile structure (Figure 8.2 (a)), In_2O_3 adopts the body-centred cubic bixbyite crystal structure (Figure 8.2 (g)) which can be viewed as a 2 ×2 ×2 supercell of the fluorite (Figure 8. 2 (e)(f)) lattice with one fourth of the anionic sites vacant.

To create the ideal structure, firstly, we created a rotated $\sqrt{2} \times \sqrt{2} \times 1$ supercell of rutile structure as shown in Figure 8.2 (b). This structure can be viewed as a distorted fluorite type along the *c* axis with a significant displacement of oxygen atoms. Secondly, we created a 2 ×2 ×2 supercell of the rotated $\sqrt{2} \times \sqrt{2} \times 1$ supercell of rutile structure as shown in Figure 8.2 (c). Now the structure can be viewed as a distorted bixbyite structure with cations lying on correlated positions. Finally, by taking into account all possible oxygen sites including original lattice sites (red balls) and interstitial sites (blue balls), the final structure (Figure 8.2 (d)) can fit in both rutile and bixbyite structures.

We then started to simulate the solid solutions of In_2O_3 and SnO_2 from the pure SnO_2 end. For each two substitutional indium cations doped onto tin ion lattice sites, a charge compensating oxygen vacancy needs to be introduced. In the created supercell (Figure 8.2 (d)), there are 32 cation and 224 oxygen sites.

The number of possible structures for the supercell that contains only one defect cluster (two substitutional indium ions and one vacancy oxygen ion) is 111,104, without taking into account symmetry. The number of possible structures increases to 1.67×10^{12} after introducing three defect clusters into the supercell.

We firstly generated ~1000 unique structures for every indium dopant concentration in the supercell of SnO_2 and performed energy optimisations using potentials listed in Table 4.1. Because the created supercell is a distorted fluorite type along the *c* axis, to provide realistic lattice sizes, we then changed the lattice parameters of the supercell with the increase of the dopant concentrations. The new lattice parameter of the supercell is determined as:

$$L_{supercell} = L_{In_2O_3} + (L_{SnO_2} - L_{In_2O_3}) \times \frac{n_{Sn}}{N_{all}},$$
(8.2)

where $L_{In_2O_3}$ is the lattice parameter of In₂O₃, L_{SnO_2} is the lattice parameter of SnO₂, n_{Sn} is the number of Sn ions and N_{all} is the total number of cation ions in the supercell.



Figure 8.2 The displacive mechanism of transition from the rutile form to the bixbyite form.
8.3 Thermal Average Lattice Properties

For the system of interest in thermodynamic equilibrium, observed properties can be calculated from our Monte Carlo sampling by

$$\langle A \rangle = \frac{\sum_{i} A_{i} \cdot \exp(-\frac{\Delta E_{i}}{kT})}{\sum_{i} \exp(-\frac{\Delta E_{i}}{kT})} \rangle, \qquad (8.3)$$

where for configuration *i* A_i is the property value that will be statistically averaged (in this case, the lattice parameter), ΔE_i is the lattice energy related the lowest lattice energy found, *T* is the temperature, and *k* is the Boltzmann constant (the difference rather than the energy itself is used to reduce numerical problems arising from summing very small numbers).

8.3.1 Supercell of bixbyite

We firstly performed the optimisation calculations under constant volume, which was followed by constant volume optimisation, for both $1 \times 1 \times 1$ and $2 \times 2 \times 2$ cells. The thermal average lattice parameter *c* is calculated at room temperature for the $1 \times 1 \times 1$ unit cell with the R1 and R2 setups using equation 8.3 and plotted in Figure 8.3 a, and for the $2 \times 2 \times 2$ supercell with the R2 setup in Figure 8.3 b. The thermal average lattice parameter *c* ± 3σ (standard derivation) for the $2 \times 2 \times 2$ supercell with the R2 setup are plotted in Figure 8.4. The full range of calculated thermal average lattice parameter *c* at 293K, 500k and 1000K can be found in Appendix B.1. The standard deviation at 293K, 500k and 1000K can be found in Appendix B.2.

The lattice parameter first increases then decreases with increasing tin dopant concentration. The expansion of the lattice at low dopant levels agree but not quantitatively with experimental results by Nadaud *et al*, [241] who found that the tin doping (up to 5-6 at.%) leads to the increase in the lattice constant. At higher doping concentration, although the lattice constants decrease with the doping concentration, the lattice still retains the bixbyite type even when there are no indium ions left in the lattice. Therefore, a more realistic structure that can fit in both rutile and bixbyite structures is required and is used in subsequent calculations.



Figure 8.3 Thermal average Lattice parameter c of solid solution of In₂O₃ and SnO₂ in supercell of bixbyite *at* 293K. (a.1×1×1 unit cell, b. 2×2×2 supercell.)



Figure 8.4 Thermal average Lattice parameter c with standard derivation of solid solution of In₂O₃ and SnO₂ in 2×2×2 supercell of bixbyite at 293K,500K and 1000K.

8.3.2 Supercell of rutile

To account for a more flexible structure in our simulation, we consider the a/c lattice parameter ratio. The value of a/c for the pure SnO₂ rutile structure is 2.08 and that of the pure In₂O₃ bixbyite structure is 1. The initial geometry optimisations over all concentrations used the rutile SnO₂ lattice parameter. The resulting value of a/c plotted in Figure 8.5a shows that there is a trend of structural change from rutile to bixbyite, with the value dropping from 2.08 to 1.53 for indium content varying from 0 at.% to 75 at.%. There is, however, still no bixbyite structure transition over the whole range. Therefore, we modified each individual initial lattice parameter based on the indium concentrations using Equation 8.2.

The resultant *a/c* lattice parameter ratio is plotted in Figure 8.5b starting from 2.08 (0 at.% Indium) which is the rutile value, reduced to 1.65-1.75 (25 at.% - 56.25 at.%), and finally decreased to 1 with the indium content increased to 75 at.%. The thermal average lattice parameters $c \pm 3\sigma$ (standard derivation) at 293K, 500k and 1000K are plotted in Figure 8.6. The full range of calculated standard deviations at 293K, 500k and 1000K can be found in Table B.5 in Appendix B.2.

As shown in Figure 8.7, the 5 most stable (lowest energy) structures out of ~1000 of 75 at.% indium concentration are defective bixbyite structures. We note that the value of a/c increases for the indium concentration over 95 at.%, which indicate that there is a problem with the IP of In₂O₃, and a large sample of random structures might be required to obtain accurate results.



Figure 8.5 Thermal average lattice parameter factor a/c of solid solution of In₂O₃ and SnO₂ in supercell of rutile. (a. original rutile lattice parameter, b. modified rutile lattice parameter using Equation 8.2.)



Figure 8.6 Thermal average lattice parameter factor a/c with standard derivation of solid solution of In_2O_3 and SnO_2 in supercell of rutile at 293K,500K and 1000K.. (modified rutile lattice parameter using Equation 8.2.)



Figure 8.7 Five lowest energy structures for the 75 at.% indium concentration.

8.4 Enthalpy of Mixing

To investigate the phase behaviour of the solid solution with SnO_2 doping into In_2O_3 , the enthalpy of mixing is calculated. The enthalpy of mixing is defined as follows:

$$\Delta E_{mix} = E_{aver} - (N \times E_{SnO_2} + M \times E_{In_2O_3})/(N + M/2), \qquad (8.4)$$

where ΔE_{mix} is the enthalpy of mixing, E_{aver} is the thermal average of total energies of mixing SnO₂ into In₂O₃, or In₂O₃ into SnO₂, E_{SnO_2} and $E_{\text{In}_2\text{O}_3}$ are the energies per formula unit of pure SnO₂ and In₂O₃, respectively, *N* and *M* are the numbers of formula units of SnO₂ and In₂O₃ contained in the supercell (*N*+*M*/2 = 32 (1×1×1 unit cell of bixbyite and supercell of rutile) or 128 (2×2×2 supercell of bixbyite)).

For SnO₂, the total lattice energy is -244.63 eV, the E_{SnO_2} is -122.31 eV. For In₂O₃, the total lattice energy is -2400.18 eV, the $E_{In_2O_3}$ is -150.01eV.

8.4.1 Supercell of bixbyite

As mentioned, in the first stage, the optimisation calculations were performed under constant volume. We then fully relaxed the structures under constant pressure. The enthalpy of mixing SnO₂ into In₂O₃ under both constant volume and constant pressure for the 1×1×1 unit cells with R1 and R2 setups are shown in Figure 8.7a, and 2×2×2 supercell with R2 setup in Figure 8.7b. The full range of calculation results including the thermal average of total energies and the enthalpy of mixing can be found in Appendices B.3 and B.4.

From the following results, we found that the mixing energy of the solid solution decreases as the defect concentration increases for both 1×1×1 and 2×2×2 cells, and there is little difference between constant volume and pressure conditions, which again suggests that the supercell we used is inappropriate.



Figure 8.8 Calculated mixing energy of solid solution of In₂O₃ and SnO₂ in supercell of bixbyite. (a.1×1×1 unit cell, b. 2×2×2 supercell.)

8.4.2 Supercell of rutile

The calculated enthalpy of mixing of solid solution of In₂O₃ and SnO₂ in a supercell of rutile using original and modified rutile lattice parameters is shown in Figure 8.8.

For the system using the original rutile lattice parameters, the mixing energy firstly increased with the defect concentration and reach 0.36 when the indium content was 18.75 at.%. The mixing energy then decreased until the indium defect concentration reached 43.75 at.%. For the system setup using the modified rutile lattice parameters, the mixing energy shows three peaks at concentrations of 18.75-25 at.%, 56.25 at.% and 87.50 at.%, and two troughs at concentrations of 43.75 at.% and 75.00 -81.25 at.%. The peak at 18.75-25 at.% represents the rutile structures, while the trough at 43.75 at.% suggests that there may exist one intermediate phase. This result gives a valuable insight into the structures of the solid solution of \ln_2O_3 and SnO_2 .



Figure 8.9 Calculated mixing energy of solid solution of In_2O_3 and SnO_2 in supercell of rutile. (a. original rutile lattice parameters, b. modified rutile lattice parameters using Equation 8.2.)

8.5 Future Work and Conclusions

The thermal average lattice structures and enthalpy of mixing of the solid solution of In₂O₃ and SnO₂ have been explored in this chapter. A supercell that can fit both rutile and bixbyite structures has been used to provide a more realistic solid solution structure. We identify that low energy structures for high indium concentration are defective bixbyite structures. However, the results of the thermal average lattice parameters show that the IP of In₂O₃ is insufficient to offer bixbyite lattice properties, which is to be expected. The calculated enthalpy of mixing suggests that there may exist one intermediate phase.

The work presented in this Chapter is a basic study for a difficult large scale project. As a preliminary work, the result gives a valuable insight into the structures of the solid solution of In₂O₃ and SnO₂. In future, the IP of In₂O₃ may need further refinement. Larger samples of random structures are required, and at least one partially ordered intermediate phase In₄Sn₃O₁₂ is worthy of study. Moreover, at greater concentrations of Sn, the switch from electronic to ionic mechanism of maintaining the charge neutrality would be of general interest for the study of the solid solution of In₂O₃ and SnO₂. The present work will, however, provide a good foundation for future study.

Chapter 9

Summary and Conclusions

In this thesis, atomistic and quantum mechanical/molecular mechanical simulation techniques have been applied to investigate the defect properties of three main TCO materials, In₂O₃, SnO₂ and ZnO.

The energetics of point defects and intrinsic disorder in In₂O₃ and SnO₂ have been calculated using the atomistic Mott-Littleton method as implemented in GULP - in the first section of results (Chapter 4). A new set of interatomic potentials was derived and applied which accurately reproduce physical and structural properties of the two binary oxides. The interatomic potential model, including a suitable approach to reproduce the fundamental band gaps, was 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. The approach will be suitable to study defects in extended systems, as the lower computational need offers significant advantages over most electronic structure techniques.

Based on the calculated point defect formation energies and lattice energies, we predict the primary type of the intrinsic disorder is the anion Frenkel pair in both binary oxide materials. In both materials, holes are unstable and tend to form point defects; electrons are stable which confirms and rationalises the *n*-type nature of these materials. The complexation of Sn with any available interstitial O will necessarily occur in Sn doped In₂O₃ under thermodynamic equilibrium at finite levels of doping, while the equilibrium shift towards electrons rather than oxygen interstitials as charge compensating species.

The intrinsic point defects in ZnO have been investigated using QM/MM embedded cluster approach using three density functionals: B97-2, PBE0 or BB1K in Chapter 5. The large calculated bulk IP indicate that the formation energy of positively charged defect will be low when the Fermi level is close to the VBM which explains the observed difficulty in p-type doping ZnO. In addition to the compact state, the defect can have a diffuse state. By considering both compact and diffuse states of the intrinsic point defects, the emission peak for the capture of a hole by the oxygen vacancy and zinc vacancy complex is 2.62 eV using BB1k, which allows us to assign this defect as the source of the blue luminescence. The red luminescence is related to the capture of a hole by the octahedral site.

Defect energies were calculated under two conditions, oxygen rich/cation poor and oxygen poor/cation rich. Under oxygen poor conditions, we found oxygen vacancies displayed the lowest formation energy which therefore likely to dominate. Under oxygen rich conditions, the dominant defect changes into zinc vacancies. The computed self-consistent Fermi energy and equilibrium defect and carrier concentrations show that ZnO is strongly *n*-type with electron concentrations greater than that of the hole concentration at high temperature and oxygen partial pressures. Oxygen vacancies are the dominant defect in ZnO under low O partial pressures.

In Chapters 6, we studied the properties of Li and H dopants in ZnO using the QM/MM embedded cluster approach. Lizn is stable in the 0 and -1 charge state, with the (-/0) transition level at 0.79 eV (B97-2) and 1.50 eV (BB1k) from the VB, which yields a deep acceptor level. The formation energy of Li_i in the +1 charge state at the octahedral site is 0.8 eV (BB1k) lower than that of tetrahedral site. The results for the Lizn-Li_{i(Oct)} defect pairs also show that the complexes with Li interstitial at the octahedral site are stable. The (+/0) transition level of both Lizn-Li_{i(Oct)} and Lizn-Li_{i(Tet)} are found to lie at 0.84 eV (BB1k) from the valence band, which yields a deep donor level. For the complexes of Lizn with Vo, the defect pair is stable in the +1 stable acting as a donor with the (+/-) transition above the CBM.

For the H related defects in ZnO, we calculated that the neutral H_i is stable at the octahedral site with the formation energy of 0.61 eV (BB1k) lower than that of tetrahedral site. In the +1 charge state, both the octahedral and tetrahedral interstitial relaxed into the antibonding site interstitial. Among four configurations, the positively charged H_i is stable at the BC_{II} site. Ho is energetically favoured compared to H_{i(BC)} with the formation energy of 0.58 eV (BB1k) lower in the positive charge state. The (+/0) transition level of Ho is 5.47 eV (BB1k) above VBM (in the CB), which will be auto-ionised. Complexes of H_i with Li_{Zn}, are also stable with H_i at the BC_{II} site and act as shallow donors in ZnO.

Intrinsic point defects in In_2O_3 have been investigated using the QM/MM embedded cluster approach using B97-2 and PBE0 density functionals in Chapter 7. Under oxygen poor conditions, we found that the indium interstitial at 16*c* site is most stable for the Fermi level within the gap using PBE0. However, using B97-2, the dominant intrinsic point defect becomes the oxygen vacancy when the Fermi level is near the CBM. Under oxygen rich conditions, the dominant point defects for both PBE0 and B97-2 become neutral oxygen split interstitials for the Fermi level close to the conduction band. From the calculated ionization energies, we found that the emission peak for capture of a hole by the +1 charge state V₀ is 2.14 eV (B97-2), and by the +2 charge state In_i at octahedral site is 2.12 eV (B97-2), which might be the source of the orange emissions.

Finally, in Chapter 8, the solid solutions of In_2O_3 and SnO_2 have been investigated using the interatomic force field from Chapter 4. The unbiased Monte Carlo method is applied to obtain random sampling results. Firstly, we randomly generated ~10,000 unique structures for ~60 out of 128 possible different tin dopant concentrations in the 2×2×2 supercells of In_2O_3 . After full relaxation, the thermal average lattice parameter still keeps the bixbyite type even though there are no remaining indium ions. A more realistic structure which can accommodate both In_2O_3 bixbyite and SnO_2 rutile crystal structures is then used. ~1000 unique structures for every indium dopant concentration in the supercell of SnO_2 have been generated. We found that the 5 most stable structures out of ~1000 of 75 at.% indium concentration are defective bixbyite structures. The calculated enthalpy of mixing of the solid solution shows three peaks which indicate that there may exist at least one intermediate phase.

In summary, the work presented in this thesis provided a detailed defect study of In₂O₃, SnO₂ and ZnO. There are several areas that would be worthy of future research.

In Chapter 5, we have studied the intrinsic point defect in ZnO. We assign the emission peak for the capture of a hole by the oxygen vacancy - zinc vacancy complex as the source of the blue luminescence; the capture of a hole by the - 2 charge state of O_i at the octahedral site as the source of the red luminescence. The transition responsible for the green luminescence (GL) was not identified. Copper, which is a natural and the most abundant impurity in ZnO was confirmed by experiment to be a prominent source of GL in this material.[169] Therefore, further QM/MM calculations on copper impurities in ZnO are needed to determine the source of the GL.

We have confirmed that the fundamental difficulty with *p* doping on ZnO arises from the instability of holes with respect to oxygen vacancies. To understand the role of impurities in ZnO, we have studied the defect properties of Li and H impurities in ZnO. More possible impurities such as N, F, AI are needed to be calculated.

It is necessary to follow on from the preliminary work on the intrinsic defects in In₂O₃ using QM/MM method in Chapter 7, as both PBE0 and B97-2 cannot reproduce good asymptotic behaviour of the Kohn-Sham potential, and a more accurate functional such as BB1k is needed to reduce the one-electron self-interaction error in the traditional DFT formulations.

Having established the preliminary study on the solid solutions In_2O_3 and SnO_2 , further work is needed to understand fully the defect properties of the solid solution. Initially, this work generated 1000 random structures for every indium dopant concentration in the supercell of SnO_2 ; larger random structures are needed to provide more accurate results. As found in experimental studies, there are two intermediate phases $In_4Sn_3O_{12}$ and In_2SnO_5 which could be investigated.

Appendices

A Sn_{In} and O_i complex binding energies in In_2O_3 .

The structures of oxygen interstitials in In_2O_3 is shown in Figure A.1. Fully range of calculation results of defect binding energies of clusters involving Sn and O interstitial complexes, including up to three interstitial O, are given in Table A.1.



Figure A.1 Interstitial oxygen in In₂O₃. The interstitial O ion is represented by green spheres, lattice O ion are represented by red spheres, first neighbour In ions are represented by blue spheres while the second neighbour In ions are represented by purple spheres.

Sn:Oi ratio	Defect cluster	Indium	Complex binding
		position	energy (eV)
1:1 [Snin•Oi]'	(Sn _{In(<i>d</i>)} •O _i)'	9	-1.54
	(Sn _{In(<i>b</i>)} •O _i)'	2	-1.19
	(Sn _{In(<i>b</i>)} -O _i)'	30	-0.93
	(Sn _{In(<i>d</i>)} -O _i)'	24	-0.85
		21	-0.67
		27	-0.80
2:1 [2Sn _{In} •O _i]×	(2Sn _{In(<i>d</i>)} •O _i)×	9,10	-2.64
	$(\operatorname{Sn}_{\operatorname{In}(b)} \bullet \operatorname{Sn}_{\operatorname{In}(d)} \bullet \operatorname{O}_{i})^{\times}$	2,9	-2.26
	$(Sn_{ln(b)} - Sn_{ln(d)} \cdot O_i)^{\times}$	30,11	-2.23
		30,10	-2.08
		30,9	-2.02
	$(Sn_{ln(d)} - Sn_{ln(d)} \cdot O_i)^{\times}$	24,9	-2.15
		24,10	-2.05
		21,10	-2.00
		27,11	-1.99
		24,11	-1.98
		27,9	-1.91
		27,10	-1.89
		21,9	-1.86
		21,11	-1.71
	$(Sn_{In(b)} - Sn_{In(b)} \cdot O_i)^{\times}$	2,30	-1.74
	$(\operatorname{Sn}_{\operatorname{In}(d)}\operatorname{-Sn}_{\operatorname{In}(b)}\operatorname{\bulletO_i})^{\times}$	2,27	-1.73
		2,24	-1.62
		2,21	-1.39
	(2Sn _{In(<i>b</i>)} -O _i)×	30,31	-1.66
	$(\operatorname{Sn}_{\operatorname{In}(b)} \bullet \operatorname{Sn}_{\operatorname{In}(d)} \operatorname{-O_i})^{\times}$	30,24	-1.58
		30,28	-1.45
		30,29	-1.45
		30,21	-1.39
		30,22	-1.39
		30,27	-1.10
		30,23	-1.04
	(2Snin(<i>d</i>) -Oi)×	30,26	-1.50
		30,25	-1.31
3:1 [3SnIn•Oi]	(3Snin(<i>d</i>)•Oi)	9,10,11	-3.31
	$(Sn_{In(b)} \bullet 2Sn_{In(d)} \bullet O_i)$	2,9,10	-2.90

Table A.1 Sn_{in} and O_i complex binding energies in In_2O_3 .

$(Sn_{In(d)} - 2Sn_{In(d)} \cdot O_i)$	9,10,24	-2.89
	9,10,26	-2.80
	9,10,25	-2.70
	9,10,21	-2.70
	9,10,28	-2.62
	9,10,29	-2.62
	9,10,22	-2.53
	9,10,27	-2.53
	9,10,23	-2.45
$(2Sn_{ln(b)} - Sn_{ln(d)} \cdot O_i)^{-}$	9,31,32	-2.55
	9,30,32	-2.49
	9,30,31	-2.36
$(Sn_{In(b)} \bullet Sn_{In(d)} - Sn_{In(d)} \bullet O_i)$	9,32,26	-2.44
	9,32,25	-2.43
	9,30,24	-2.40
	9,31,24	-2.38
	9,31,25	-2.36
	9,32,24	-2.34
	9,32,21	-2.31
	9,32,27	-2.30
	9,31,22	-2.29
	9,32,28	-2.29
	9,31,29	-2.25
	9,30,22	-2.23
	9,30,29	-2.19
	9,32,23	-2.17
	9,31,27	-2.14
	9,30,26	-2.14
	9,30,21	-2.11
	9,32,22	-2.10
	9,30,28	-2.09
	9,32,29	-2.05
	9,30,25	-2.03
	9,31,26	-2.02
	9,31,23	-2.01
	9,31,21	-1.83
	9,31,28	-1.80
	9,30,27	-1.76
	9,30,23	-1.67
		-

$(2Sn_{\ln(d)} - Sn_{\ln(d)} \bullet O_i)^{\cdot}$	9,24,25	-2.37
	9,29,24	-2.35
	9,27,24	-2.31
	9,24,26	-2.30
	9,29,25	-2.29
	9,28,24	-2.27
	9,25,26	-2.22
	9,29,26	-2.21
	9,28,25	-2.19
	9,22,26	-2.19
	9,27,25	-2.17
	9,27,26	-2.14
	9,29,22	-2.13
	9,21,25	-2.12
	9,28,22	-2.11
	9,28,26	-2.07
	9,23,24	-2.07
	9,22,24	-2.06
	9,29,21	-2.05
	9,21,22	-2.02
	9,27,21	-2.00
	9,22,25	-1.94
	9,29,23	-1.94
	9,21,24	-1.92
	9,28,21	-1.92
	9,22,23	-1.87
	9,27,29	-1.87
	9,28,29	-1.87
	9,27,28	-1.81
	9,28,23	-1.80
	9,27,23	-1.78
	9,21,26	-1.78
	9,21,23	-1.76
	9,23,25	-1.68
	9,23,26	-1.64
(3Snin(<i>b</i>) -Oi)	30,31,32	-2.18
$(2Sn_{in(b)} \bullet Sn_{in(d)} - O_i)$	30,31,24	-2.01
	30,31,29	-1.90
	30,31,22	-1.89

	00.01.05	1.010
	30,31,25	-1.819
	30,31,26	-1.9
	30,31,21	-1.55
	30,31,27	-1.54
	30,31,23	-1.54
$(2Sn_{In(d)} - Sn_{In(b)} \cdot O_i)$	2,27,24	-1.96
	2,27,26	-1.95
	2,27,25	-1.92
	2,27,28	-1.81
	2,24,25	-1.77
	2,27,21	-1.72
	2,27,22	-1.70
	2,27,23	-1.64
	2,21,25	-1.60
	2,21,26	-1.35
	2,21,22	-1.32
	2,21,24	-1.30
$(Sn_{ln(b)} \bullet 2Sn_{ln(d)} - O_i)^{\cdot}$	30,24,26	-1.85
	30,24,25	-1.66
	30,25,26	-1.59
	30,21,22	-1.57
	30,27,24	-1.56
	30,21,25	-1.52
	30,28,29	-1.51
	30,21,24	-1.49
	30,27,26	-1.45
	30,21,26	-1.42
	30,27,21	-1.35
	30,27,22	-1.32
	30,21,23	-1.23
	30,27,25	-1.23
	30,22,23	-1.22
	30,27,29	-1.15
	30,27,28	-1.14
	30,27,23	-0.91
(3Sn _{In(d)} -O _i) ⁻	24,25,28	-1.83
	24,25,27	-1.80
	24,25,29	-1.79
	24,25,26	-1.72

		27,22,26	-1.67
		27,21,25	-1.66
		27,28,24	-1.60
		27,28,25	-1.56
		27,28,26	-1.56
		21,22,27	-1.44
		27,21,26	-1.40
		21,22,28	-1.39
		27,22,24	-1.38
		27,21,24	-1.38
		27,28,22	-1.37
		21,22,29	-1.36
		24,25,23	-1.35
		24,25,21	-1.32
		27,28,21	-1.32
		27,22,25	-1.31
		27,28,23	-1.29
		27,23,26	-1.29
		27,23,25	-1.28
		21,22,23	-1.22
		21,22,26	-1.18
		21,22,25	-1.16
		24,25,22	-1.02
		27,28,29	-1.01
		21,22,24	-0.87
4:1 [4Sn _{In} •Oi]	$(\operatorname{Sn}_{\operatorname{In}(b)} \bullet \operatorname{3Sn}_{\operatorname{In}(d)} \bullet \operatorname{O}_{i})^{\cdots}$	2,9,10,11	-3.12

B Solid Solution of In₂O₃ and SnO₂ Results

B.1 Thermal Average Lattice Parameters

Table B.1 Calculated thermal average lattice parameters of solid solution of In_2O_3 and SnO_2 in 111 unit cell of In_2O_3 under constant volume.

Number of Sn _{in}	Thermal average lattice parameters (Å)					
			constan	t volume		
	293	3 K	50	0 K	100	00 K
	R1	R2	R1	R2	R1	R2
2	10.1990	10.1333	10.1990	10.1332	10.1990	10.1376
4	10.2005	10.135	10.2005	10.135	10.2005	10.1472
6	10.2034	10.1484	10.2034	10.1482	10.2034	10.1527
8	10.1797	10.1578	10.1797	10.1578	10.1797	10.1564
10	10.1720	10.1474	10.1720	10.1474	10.1720	10.1559
12	10.1863	10.1605	10.1863	10.1594	10.1863	10.1543
14	10.1512	10.1446	10.1512	10.1446	10.1512	10.1493
16	10.1546	10.1507	10.1546	10.1507	10.1545	10.1451
18	10.1344	10.1379	10.1344	10.1379	10.1345	10.1378
20	10.1344	10.1323	10.1344	10.1323	10.1344	10.1316
22	10.1310	10.1234	10.1310	10.1234	10.1309	10.1239
24	10.1148	10.1155	10.1148	10.1155	10.1149	10.1163
26	10.1101	10.1061	10.1101	10.1061	10.1104	10.1092
28	10.1089	10.1078	10.1089	10.1077	10.1089	10.1041

Number of Snin	Thermal average lattice parameters (Å)			
	constant volume			
	293 K	500 K	1000 K	
20	20.2742	20.2742	20.2741	
30	20.2885	20.2882	20.2879	
40	20.2919	20.2919	20.2919	
50	20.2957	20.2957	20.2956	
60	20.2942	20.2942	20.2942	
70	20.2984	20.2984	20.2986	
80	20.2971	20.2971	20.2971	
90	20.2906	20.2906	20.2906	
100	20.2808	20.2808	20.2808	
110	20.2679	20.2679	20.2679	
120	20.2541	20.2541	20.2541	
130	20.2566	20.2565	20.2561	
140	20.2584	20.2584	20.2584	
150	20.2272	20.2272	20.2272	
160	20.2210	20.2210	20.2210	
170	20.2174	20.2174	20.2174	
180	20.2044	20.2044	20.2044	
200	20.1960	20.1960	20.1960	
210	20.1920	20.1920	20.1920	
220	20.1827	20.1831	20.1842	
230	20.1907	20.1907	20.1907	
240	20.2001	20.2001	20.2001	

Table B.2 Calculated thermal average lattice parameters of solid solution of In_2O_3 and SnO_2 in 222 supercell of In_2O_3 under constant volume.

B.2 Standard Deviation

Number	standard deviation at room temperature					
of Sn _{In}						
	constant	t volume	constant	pressure		
	R1	R2	R1	R2		
2	0.0000E+00	1.4061E-03	2.1431E-02	7.3306E-04		
4	0.0000E+00	1.6503E-02	5.2858E-05	6.6456E-03		
6	3.0518E-05	4.9679E-04	1.6514E-02	8.8678E-03		
8	4.3158E-05	1.0866E-02	4.0053E-03	1.1852E-02		
10	0.0000E+00	1.0136E-02	6.1035E-05	2.0613E-02		
12	0.0000E+00	N/A	2.2406E-02	7.4465E-03		
14	0.0000E+00	N/A	8.6317E-05	N/A		
16	4.3158E-05	N/A	6.1035E-05	4.4664E-03		
18	4.3158E-05	N/A	0.0000E+00	N/A		
20	0.0000E+00	6.2840E-04	6.5025E-04	7.2520E-03		
22	6.6721E-04	9.8794E-04	4.3158E-05	5.2148E-04		
24	1.0420E-02	1.6765E-02	0.0000E+00	2.3651E-03		
26	1.8407E-03	N/A	0.0000E+00	3.4527E-04		
28	4.3986E-03	3.9612E-03	4.9894E-03	1.3641E-02		

Table B.3 Calculated standard deviation of solid solution of In_2O_3 and SnO_2 in 111 unit cell of In_2O_3 at room temperature.

number of Snin		standard deviation			
	293 K	500 K	1000 K		
20	2.0305E-05	1.5353E-04	6.3959E-04		
30	8.0956E-04	1.0356E-03	1.1427E-03		
40	0.0000E+00	0.0000E+00	4.1292E-07		
50	1.7026E-06	5.5529E-05	6.5349E-04		
60	0.0000E+00	0.0000E+00	2.3833E-07		
70	4.1383E-05	2.6558E-04	9.6154E-04		
80	N/A	N/A	2.3833E-07		
90	N/A	N/A	N/A		
100	N/A	2.3833E-07	2.3833E-07		
110	N/A	N/A	N/A		
120	N/A	N/A	N/A		
130	1.4972E-04	5.9001E-04	1.4109E-03		
140	0.0000E+00	0.0000E+00	6.3079E-07		
150	8.2589E-07	3.7454E-05	5.2748E-04		
160	2.3833E-07	0.0000E+00	4.7686E-07		
170	N/A	N/A	2.3833E-07		
180	N/A	N/A	N/A		
190	N/A	N/A	3.4385E-06		
200	N/A	N/A	N/A		
210	N/A	N/A	N/A		
220	8.1313E-04	1.9354E-03	3.1484E-03		
230	0.0000E+00	0.0000E+00	2.3833E-07		
240	2.3833E-07	1.0115E-06	6.7304E-05		

Table B.4 Calculated standard deviation of solid solution of In_2O_3 and SnO_2 in 222 supercell of In_2O_3 under constant volume (R2) at 273K, 500K and 1000K.

number of Insn	standard deviation				
	293K	500K	1000K		
0	1.9774E-07	1.9774E-07	1.9774E-07		
2	3.1245E-03	3.3391E-03	3.9699E-03		
4	6.5911E-03	7.9114E-03	8.2231E-03		
6	5.7559E-07	5.2992E-05	2.4234E-03		
8	2.3721E-02	3.2604E-02	3.7536E-02		
10	N/A	2.0000E-08	1.8573E-06		
12	6.2665E-04	1.6889E-03	3.0105E-03		
14	4.7681E-03	9.6379E-03	1.4001E-02		
16	5.1788E-07	3.7222E-05	7.6384E-04		
18	2.5377E-07	8.5532E-05	5.2590E-03		
20	3.1111E-06	1.1930E-04	1.6817E-03		
22	N/A	2.3173E-07	6.5585E-05		
24	N/A	1.0000E-08	7.1872E-06		
26	N/A	1.4142E-08	3.7435E-06		
28	N/A	N/A	6.1349E-06		
30	N/A	N/A	1.4142E-0		
32	3.1916E-06	1.0835E-04	1.3041E-03		

Table B.5 Calculated standard deviation of solid solution of In_2O_3 and SnO_2 in supercell of rutile at room temperature.

B.3 Thermal Average Lattice Energies

Number of Snin	Thermal average lattice energy (eV)			
	constant volume		constant pressure	
	R1	R2	R1	R2
2	-2482.02	-2496.63	-2484.32	-2497.07
4	-2581.21	-2594.56	-2583.65	-2593.85
6	-2677.77	-2690.91	-2680.14	-2691.06
8	-2775.44	-2788.12	-2778.98	-2788.61
10	-2876.31	-2885.24	-2877.72	-2884.93
12	-2975.04	-2981.89	-2977.72	-2982.58
14	-3073.37	-3080.23	-3074.37	-3081.00
16	-3172.70	-3178.21	-3178.04	-3177.88
18	-3272.14	-3276.14	-3276.53	-3277.48
20	-3371.45	-3375.21	-3370.65	-3375.38
22	-3471.47	-3473.65	-3471.73	-3473.52
24	-3571.72	-3572.53	-3571.08	-3572.77
26	-3672.57	-3673.58	-3673.23	-3673.47
28	-3773.58	-3773.75	-3773.55	-3773.62

Table B.6 Calculated mixing energy of solid solution of In_2O_3 and SnO_2 in 111 unit cell of In_2O_3 .

Number of Snin	Thermal average lattice energy		
	constant volume	constant pressure	
10		-19682.76	
20	-20163.04	-20165.46	
30	-20644.64	-20646.66	
40	-21129.40	-21129.28	
50	-21612.60	-21611.32	
60	-22096.22	-22094.04	
70	-22577.50	-22582.67	
80	-23064.36	-23067.43	
90	-23553.82	-23546.09	
100	-24038.78	-24034.60	
110	-24525.97	-24524.55	
120	-25016.34	-25013.99	
130	-25497.43	-25498.45	
140	-25990.95	-25989.14	
150	-26483.82	-26483.49	
160	-26976.00	-26978.49	
170	-27471.80	-27472.70	
180	-27972.21	-27976.18	
200	-28969.54	-28971.26	
210	-29470.58		
220	-29973.92		
230	-30484.94		
240	-30997.45		

Table B.7 Calculated mixing energy of solid solution of In_2O_3 and SnO_2 222 supercell (R2).

B.4 Enthalpy of Mixing

Number of Snin	Enthalpy of mixing (eV)			
	constant volume		constant pressure	
	R1	R2	R1	R2
2	0.40	-0.06	0.33	-0.07
4	0.26	-0.16	0.18	-0.14
6	0.20	-0.21	0.12	-0.22
8	0.10	-0.30	-0.01	-0.31
10	-0.09	-0.37	-0.14	-0.36
12	-0.22	-0.44	-0.31	-0.46
14	-0.34	-0.55	-0.37	-0.58
16	-0.49	-0.66	-0.65	-0.65
18	-0.64	-0.76	-0.77	-0.80
20	-0.78	-0.90	-0.76	-0.91
22	-0.95	-1.02	-0.96	-1.02
24	-1.13	-1.15	-1.11	-1.16
26	-1.32	-1.35	-1.34	-1.35
28	-1.52	-1.53	-1.52	-1.52

Table B.8 Calculated mixing energy of solid solution of In_2O_3 and SnO_2 in 111 unit cell of In_2O_3 .

Number of Snin	Enthalpy of mixing (eV)		
	constant volume	constant pressure	
10		-0.03	
20	-0.06	-0.07	
30	-0.09	-0.10	
40	-0.14	-0.14	
50	-0.18	-0.17	
60	-0.22	-0.21	
70	-0.25	-0.27	
80	-0.31	-0.32	
90	-0.37	-0.34	
100	-0.42	-0.40	
110	-0.47	-0.46	
120	-0.54	-0.53	
130	-0.57	-0.57	
140	-0.65	-0.64	
150	-0.73	-0.72	
160	-0.80	-0.81	
170	-0.89	-0.89	
180	-1.00	-1.01	
200	-1.20	-1.20	
210	-1.31		
220	-1.42		
230	-1.57		
240	-1.73		

Table B.9 Calculated mixing energy of solid solution of In_2O_3 and SnO_2 222 supercell (R2).

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