# Synthesis and Characterisation of Group 15-containing Inorganic Solids for Energy Conversion Applications

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## Declaration

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

#### Abstract

The increasing demand for and awareness of sustainable energy resources has encouraged the search for new materials in energy conversion applications, in particular, solar absorber materials, transparent-conducting oxides and thermoelectrics. The primary requirements for these novel materials are high earth-abundancy, non-toxicity, low cost and suitable adaptability in their respective applications. In this thesis, novel metal oxide and sulphide materials will be explored through various experimental characterisation techniques such as X-ray diffraction, X-ray photoelectron spectroscopy, ultraviolet-visible light spectroscopy and energy dispersive spectroscopy to investigate their structural and physical properties. These metal oxide materials are novel in their application fields, which include sodium antimony sulphide NaSbS<sub>2</sub>, barium bismuth oxide BaBi<sub>2</sub>O<sub>6</sub>, gallium antimony oxide GaSbO<sub>4</sub>, ZnSb<sub>2</sub>O<sub>6</sub> and various trivalent metalion doped ZnSb<sub>2</sub>O<sub>6</sub>. Experimental results will be discussed in conjunction with theoretical data obtained by Scanlon Materials Theory Group, and analysed to provide a detailed breakdown on the suitability of these metal oxide materials in becoming potential materials in their own fields. Furthermore, the cation ordering of GaSbO<sub>4</sub> and various metal-ion doped ZnSb<sub>2</sub>O<sub>6</sub> will be investigated through the changes in their structural and electronic properties in order to understand the doping mechanism and the role of dopant in these doped materials. These GaSbO<sub>4</sub> doped ZnSb<sub>2</sub>O<sub>6</sub> materials are potential candidates for transparent-conducting oxide and thermoelectric applications.

### **Impact Statement**

Due to increasing environmental awareness and desire to replace fossil fuels, alternative energy sources such as solar energy have been widely considered, from silicon solar panel to Tesla solar roof. Because of this, there is also a rising demand for better and more efficient solar panels, this has initiated interests in finding and making the next generation solar absorber materials. This project will partially focus on these potential solar absorber materials, transparent conducting oxides and thermoelectric materials through computational screening and experimental synthesis. The primary focus of this project will be placed on materials with high earth abundancy, non-toxicity and low production cost to enhance current materials and advance the development of renewable energy resources. By doing so, we hope to identify materials that could demonstrate the desired properties and thus, a potential in becoming a better solar absorber material. Unlike fossil fuels, solar energy is unlimited and requires significantly less energy to manufacture and operate, it is also more carbon-friendly, which could minimise the impact on global warming. While silicon, the most commercialised solar panel material, is earth abundant, costs associated with extraction and operation of metal components is relatively high. For this reason, with more new potential solar absorber materials becoming available on the commercial market, this would lower the costs whilst providing alternatives to the public domain. Similarly, finding new potential transparent conducting oxides will allow materials with high efficiency and better properties to be identified. As a solar cell is made up of different components including the transparent conducting oxide layer, this would enable a high solar efficiency in the overall solar cell. Another part of the project is to investigate new thermoelectric materials, although these materials are not as widely known to the public as solar absorbers, thermoelectric materials can scavenge waste heat and turn it into useful energy. Because of this attractive feature, we hope to find alternative thermoelectric materials that are more efficient across a wide temperature range whilst overcoming technological challenges in current materials. Researching for alternative energy storage materials will hopefully raise awareness and encourage the general public to use renewable energy resources as much as possible, and this, on many levels, will benefit the environment and society, driving us towards a more carbon-neutral future. Additionally, the research community will also benefit from the broad scope of promising materials and therefore, presenting more innovations and ideas in each subsequent field. In order to help accurately identify potential energy storage materials, computational screening will also be performed using hybrid Density Functional Theory (DFT) in collaboration with Scanlon Materials Theory Group in this project.

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## **Chapter 1**

## Introduction

There has been an increasing interest over the last few decades in developing alternative renewable energy resources to combat the limited supply of fossil fuel and subsequent global environmental impacts.<sup>1–3</sup> There are many ways to generate safe energy from sustainable resources, which include harnessing energy directly from the sun and scavenging waste heat into electricity by means of thermoelectric devices.<sup>4,5</sup> Solar energy has attracted a lot of attention as being one of the most promising and viable alternative energy resource.<sup>6,7</sup> Likewise, thermoelectric materials have also been widely investigated and together could provide a sustainable clean energy solution.<sup>8</sup>

### 1.1 Basics of Electronic Structure of Solids

Electrons in a single isolated atom occupy atomic orbitals, of which each has a discrete energy level, these atomic orbitals overlap when two atoms join together. Upon the joining of two atoms, each atomic orbital splits into two molecular orbitals of different energy in accordance with Pauli exclusion principle. When a large number (N) of atoms join together to form a solid, the atomic orbitals overlap with one another. Each of these atomic orbital then splits into N discrete molecular orbitals with different energy levels due to Pauli exclusion principle. Since there is a large number of atoms in a solid, the corresponding number of orbitals is also very large and thus these orbitals are very closely spaced in energy. As a result, the energy of adjacent levels is so close



together that they can be considered to be a continuum, forming an energy band.

Figure 1.1: A diagram demonstrating the electron structure of an insulator, a semiconductor and conductor.

Energy bands formed in a solid are called the valence band and conduction band. The alignment and position of these bands vary accordingly in different solids, conduction band in general is higher in energy than valence band. Figure 1.1 shows the conduction band and valence band positions in an insulator, semiconductor and conductor respectively. In an insulator, the conduction band and valence band, so the large energy gap between conduction band and valence band is known as the band gap, E<sub>g</sub>. The large band gap prevents any transition of electrons from the valence band to the conduction band, thus insulators are electrically non-conductive. Semiconductors have a smaller band gap than insulators whereas band gap is absent in conductors as the valence band and conduction band are completely overlapped with one another. In addition, electrons in the valence band of a semiconductor material can be promoted to the conduction band across the band gap upon the absorption of light or thermal energy, leaving a hole behind in the valence band, enabling them to be conductive. While for conductors, delocalized electrons can move freely across the bands and therefore they are highly conductive.



Figure 1.2: A diagram demonstrating the electron structure of a n-type semi-condcutor and p-type semiconductor.

As the atoms in a solid are very closely packed together and the interatomic separation is equivalent to the size of atoms, discrete energy levels of free atoms are broadened into electronic bands mostly due to the strong overlapping and interaction between outer orbitals of the atoms. Subsequently, these infinite number of energy levels form into a continuum, making up the conduction band and valence band of a solid, which is illustrated in Figure 1.3.





Semiconductors are one of the mostly researched topics worldwide due to their highly tunable structural, optical and electronic properties. They are commonly found in many

applications today, ranging from personal electronic devices to industrial applications. Silicon is a classic example of a semiconducting material, pure silicon is not very conductive due to the fact it has an indirect band gap (1.1 eV) and a relatively low carrier concentration of about  $1 \times 10^{10}$  cm<sup>3</sup>. More details will be explored in subsequent sections. For this reason, much effort has been raised in order to improve the conductivity of silicon, one of the most prominent attempts includes the introduction of impurities such as dopants into the crystal structure. Common dopants are vastly trivalent and penta-valent elements, such as boron, phosphorus, aluminium, indium and antimony. Boron and phosphorus are the most commonly used choice of dopants in silicon doping. There are two types of doping chemistry, namely n-type and p-type doping, electron-rich dopants relative to silicon such as penta-valent elements fall into n-type doping whilst electron-deficient elements such as tri-valent elements fall into p-type doping. Figure 1.2 illustrates the different types of doping mechanisms and the relative movement of electrons in terms of energy band diagrams. In n-type doping, the penta-valent dopant has an additional electron in the outermost shell than silicon, this additional outer electron is delocalised and serves as the majority charge carrier in the crystal lattice. As a result, delocalised electrons within the lattice would contribute to the formation of a high energy level located close to the conduction band and far away from the valence band, which is also known as the electron donor level. The Fermi level, defined as the highest energy state occupied by electrons at 0 K, is also shifted so it is roughly halfway between the electron donor level and the conduction band. Therefore, electrons can now be excited into the conduction band with much less energy in comparison to the intrinsic electrons in undoped silicon. In contrast to n-type doping, holes are created as the majority charge carriers in p-type doping and tri-valent dopants are known as electron acceptors. Since they have fewer outer electrons than silicon, an outer electron will be transferred from silicon to boron, this will create a hole in the valence band of silicon. The hole formation allows a new energy level, the electron acceptor level, to be created and it lies closer to the valence band than conduction band. Electrons can then be easily excited from the valence band into the electron acceptor level, thus leaving delocalized holes in the valence band. As

a result, the Fermi level is also shifted to the midpoint between the electron acceptor level and the valence band. Whether a material is n-type or p-type semiconductor solely depends on the majority charge carriers present in the lattice as n-type and ptype semiconductor corresponds to having electrons and holes as the majority charge carriers respectively.

The formation of delocalised electrons and holes in dopant chemistry is considered to be a form of defect being introduced to perturb the crystal lattice in order to improve the electrical conductivity of a semiconductor material. Other forms of defects include substitutional and interstitial defects, vacancies. An overall electroneutrality is always retained in the lattice despite n-type or p-type doping is involved in the process.

As electrical conductivity is proportional to the product of charge carrier mobility and concentration, it is important to understand the factors impeding these two quantities. Charge carrier mobility is defined by how quickly a charge carrier, which can be either an electron or a hole, moves through a semiconductor in presence of an electric field. At very high charge carrier concentration, mobility is usually limited and thus impacting the conductivity. While at very low charge carrier concentration with a high carrier mobility, the conductivity is also limited. In addition, charge carrier mobility decreases with increasing temperature. Therefore, a maximal conductivity is usually obtained at an optimal charge carrier concentration of  $10^{20} \,\mathrm{m}^{-3}$  together with a decent carrier mobility.

### **1.2 Optical Properties of Solids**

When a light beam is incident on an optical medium, it can either reflect, propagate and transmit through a solid state material. Whilst the light is propagating through the material, it can be refracted, absorbed, luminesced and scattered. In particular, the absorption of light by an optical medium is usually quantified by its absorption coefficient  $\alpha$ . It is the fraction of the power absorbed in a unit length of the medium and the intensity of light beam at position *z* can be represented by *l*(*z*) while the light beam is propagating in the *z* direction. Hence, the Beer-Lambert law can be derived as follow:

$$I(z) = I_0 e^{-\alpha z}$$

where  $I_0$  is the optical intensity at z=0.



Figure 1.4: A diagram illustrating the interband transition in semiconductors and insulators.

Semiconductors and insulators typically have a fundamental absorption edge in the near-infared, visible or ultraviolet spectral region. The absorption edge is caused by the onset of optical transitions across the fundamental band gap of the material. Optical transitions occur when electrons are excited between the electronic bands of a material, this process is also known as the interband absorption. As mentioned in the previous chapter, an electron will be promoted across the band gap of a material by absorbing a photon during an optical transition. This transition can only occur if an electron is present in the initial state in the lower band and final state in the upper band must be empty according to Pauli exclusion principle. A classic example will be the transition across the fundamental band gap of a semiconductor or insulator material, where an electron is excited from the filled valence band to the empty conduction band upon absorbing a photon, as shown in Figure 1.4. However, the excitation of the electron will leave the initial state of the lower energy band unoccupied, a hole is then created to accompany the electronic transition. This phenomenon is also known as the creation of an electron-hole pair. The strength and likelihood of an interband

transition is dependent on the initial and final electronic states of the energy bands, for example in GaAs, the band absorption is considered to be relatively strong as the electrons transition from the *p*-like valence band maximum to *s*-like conduction band minimum.<sup>9–11</sup> In addition, the transition from *p* to *s* states are electric-dipole allowed and in compliance with the dipole transition rule.<sup>12,13</sup>

In order to understand the direct band absorption in semiconductors like GaAs, the band structure, illustrated in Figure 1.5, is being brought into context along with the principle of Brillouin zones. The set of points closer to the origin than to any other reciprocal lattice points within a crystal lattice is defined as a Brillouin zone and these set of vector points are enclosed by the Bragg planes. The first Brillouin zone is simply the smallest volume, also known as the region in k-space, entirely enclosed by Bragg planes of the reciprocal lattice closest to the origin. Electrons can occupy the first kspace without being diffracted whilst electrons can move in the x and y directions in the second Brillouin zone. Note that k is the wave factor. There are more than one Brillouin zones and it increases with the increasing distances from the origin. The zone center which is also the origin where k is (0, 0, 0) is known as the  $\Gamma$  point whereas the zone edges along the (100) and (111) directions are called the X and L points respectively.<sup>10</sup> In GaAs, the direction transition occur at  $\Gamma$  point where k=0, the maxima of the valence band and the minima of the conduction band both occur at this point and thus allow a direct transition to occur. The band gap is therefore denoted by being the shortest distance between the conduction band minimum and valence band maximum, at which a direct transition occurred, in a band structure diagram.



Figure 1.5: Band Structure of GaAs with spin-orbit coupling (top) and without spin-orbit coupling (below). Courtesy of Dr John Buckeridge in SMTG.

Overall, the interband absorption in solids can be summarized into two main categories: materials with a direct band gap and materials with an indirect band gap.

Silicon is the most widely used indirect band gap material in solar cells and other semiconductor applications, therefore it is essential and important to understand how the optical properties behave in indirect band gap materials. In contrast to materials with a direct band gap, phonons are often involved in an indirect optical transition. As the conduction band minimum of indirect band gap semiconductors are located away from  $\Gamma$  point, a phonon must be involved in the band edge absorption in order to observe the overall momentum. Germanium is a typical example of such material where the conduction band minimum occurs at L point, therefore the indirect band gap

transition also occurs at L point. Despite the presence of phonon absorption, it only accounts for a very small amount of energy in the overall transition.

### **1.3 Density Functional Theory**

The band structure diagram mentioned in the previous section is usually simulated by density functional theory (DFT), in which DFT has been widely used in various scientific sectors to predict structures, chemical, optical, spectroscopic and thermodynamic properties in materials science as well as biological sciences. Most fundamental properties of a material, such as structural and optical properties, can be derived from the electronic structure of the material, enabling *ab* initio simulations to probe into the electronic structure of a material with predictive accuracy. Therefore, modern DFT technique is a well-equipped tool in predicting theoretical properties in material design, and allowing a comprehensive analysis of both theoretical and experimental results.

A full quantum-mechanical treatment of a material would typically require the calculation of the system's many-nuclei, many-electron wave function. However, their behaviour is decoupled from the electrons in the vast majority of simulations due to the relatively large mass of the nuclei. In this case, they may be treated as classical pointlike particles (the Born–Oppenheimer approximation) instead. In contrast to the nuclei, a full quantum-mechanical treatment is required in order to understand their behaviour due to the low mass of electrons. As a consequence, it is challenging to achieve an accountable solution because of the computational complexity of the multi-body Schrödinger equation. DFT, on the other hand, provides a viable alternative solution to this complex computational problem by focussing on the electron density of a system, it can also model the properties of a multi-electron system, i.e the electronic structure which is also known as the ground state structure. In addition, the total energy of the system is independent of the electron density.<sup>14,15</sup>

DFT was first successfully transformed by Kohn and Sham to solve a set of independentparticle equations, which were much easier to solve than the original multi-body problem.<sup>16</sup> Functionals are functions of another functions explicitly used in DFT modelling, in Kohn and Sham's case, a functional called the exchange-correlation (XC) potential was introduced and it is still commonly applied amongst DFT users today. The other reason leaning towards the success of DFT and its popular usage in the scientific community is the relatively low computational costs compared to traditional methods such as Hartree-Fock theory. Hartree-Fock theory is fundamentally at the heart of the electronic structure theory and the basis of molecular orbital theory, in which the molecular orbital theory describes an individual electron's motion by a single-particle function independent on the instantaneous motions of surrounding electrons.<sup>17</sup> It has been commonly applied in deriving the solution of the Schrödinger equation for atoms, molecules, nano-structures and solids since its first appearance.

DFT provides a fast and reliable method to determine the electronic structure of a material, however, the accuracy is still somewhat lacking due to the fact that DFT and many other computational modelling methods are just approximations. Therefore, there has been a concentrated amount of effort to modify the functionals in DFT in order to improve accuracy. Despite the lack of high accuracy in DFT, theoretical data computed via DFT is usually comparable with the experimentally derived data, it is particularly useful in estimating different properties of a material. While the theoretical data may not always perfectly match up with the experimental results, the discrepancy, however, will allow further investigation into the atomic arrangement and other relevant properties of the material. Hence, this will likely derive an explanation to account for the discrepancy. Therefore, it is also important for researchers to keep an open mind whilst comparing theoretical and experimental data to ensure optimal objectiveness. Moreover, DFT can be used to predict various possible doping mechanisms of a material, providing detailed insights on the structural and electronic properties in experimental chemistry.

### 1.4 Photovoltaic Materials

A solar cell is a device that can directly transform sunlight into electricity and the absorber layer is one of the key components in assembly of a photovoltaic device. A simple semiconductor-based solar cell contains two electrodes: one usually is a transparent conducting oxide (TCO) on glass and the other is metal backing; a p-n junction, which often contains the photovoltaic material, is sandwiched between the two electrodes which allows the generation of electron-hole pair upon irradiation by photons. As a result, the electron will diffuse through the n-type semiconductor to the metal electrode while the hole travels through the junction and reaches the p-type material. An electric current is produced when the electron follows the short circuit and recombines with a hole at the TCO electrode, with the two electrodes connected.





Extensive studies have been carried out to investigate various potential solar absorber materials, that can be modified accordingly to maximize the efficiency of the cell. Ideal candidates for solar absorber materials should possess optical band gaps between 1.1 eV and 1.6 eV, as predicted by the Shockley-Queisser limit, <sup>18</sup> to optimize their solar absorption. Of course, such candidates should also be highly earth-abundant, low cost and highly biocompatible to minimise harmful effects to the environment. Additionally, it is desirable for solar absorber materials to have high charge carrier mobilities, which is dependent on the dispersion of band edges in a material and in theory is quantified by the effective mass of a carrier. Thus, high carrier mobilities can be achieved by having a high dispersion of band edges and smaller effective masses.<sup>19</sup> However, the

carrier mobility is limited by various means of scattering: defects, phonons and other charge carriers.



Figure 1.7: Diagram showing (a) the ideal IV curve and the power curve of solar cell and (b) the maximum voltage and current ( $V_{max}$  and  $I_{max}$ ) at the maximum power output, and the shaded area under the IV curve representing the fill factor of a solar cell.

To determine the performance of a solar cell, there are a few parameters that need to be taken into consideration: short-circuit current density ( $J_{SC}$ ), open-circuit voltage ( $V_{OC}$ ) and fill factor (FF). Short-circuit current is more commonly known as the short-circuit current density, which is independent of the cell area, it measures the electric current produced by the recombination of charge carriers when there is no voltage applied across the cell, which is shown in Figure 1.7(a). Open-circuit voltage, also shown in the same figure, measures the power of recombination in the solar cell, maximum open-circuit voltage is achieved when the net current through the cell is zero.<sup>20,21</sup> In Figure 1.7(b), the shaded area under the IV curve is the graphical quantification of the fill factor, which is interdependent on  $V_{OC}$  and  $I_{SC}$ , and it determines the maximum power from a solar cell.<sup>22</sup>

As shown in Figure 1.8, having a close band alignment of the absorber layer with its

neighbouring materials is advantageous as the loss of  $V_{OC}$  can be minimized with an efficient band alignment which in turn enhances the carrier transport throughout the cell. The band positions can often be adjusted by doping to achieve a close band alignment between the materials in a solar cell.



Figure 1.8: A diagram showing the band alignment in a heterojunction solar cell showing the conduction band minimum (CBM), valence band minimum (VBM), hole transporting material (HTM), Fermi-level of n-type transparent conducting oxide and p-type HTM.<sup>19</sup>

#### 1.4.1 First generation solar cells: silicon

Owing to its high earth abundancy, non-toxicity, stable cell efficiency and well-established silicon-wafers technology, crystalline silicon (c-Si) has been dominating the commercial solar cell market since the development of new photovoltaic materials.<sup>23,24</sup> There has been a tremendous amount of effort worldwide in optimizing the band gap and conversion efficiency of such cells, mostly by doping crystalline silicon with various Group 13 or Group 15 elements to achieve p-type or n-type conductivity. Recently, a solar cell composed of crystalline silicon sandwiched between an amorphous silicon (a-Si) and a mixed n-type/p-type a-Si layers was reported to have a ground-breaking photoconversion efficiency of 26.3%, reaching towards the theoretical conversion efficiency limit of silicon solar cells.<sup>25</sup> Despite the many advantages of silicon solar cells,

the high production cost and necessarily large feedstock of silicon will remain a critical issue due to the efficiency being significantly limited by the energy difference between its direct and indirect band gap.<sup>23,26–28</sup> Furthermore, waste heat produced in silicon-based solar cells is another issue in large scale use of such solar cells. Are there any better alternatives that can overcome all these adverse effects?

#### 1.4.2 Second generation solar cells: thin film alternatives

One of the alternatives is thin film solar cells composed of CdTe and Cu( $\ln_xGa_{1-x}Se_2$ ) (CIGS), both have been reported to have a remarkably improved conversion efficiency of ~22% in recent studies.<sup>29–31</sup> In contrast to crystalline silicon-based solar cells, CdTe and CIGS typically have an optical indirect band gap of ~1.5 eV and high absorption coefficients of ~10<sup>5</sup> cm<sup>-1</sup>, allowing optimal absorption of solar radiation.<sup>32</sup> Moreover, CdTe and CIGS thin films are more heat resistant, flexible and their overall costs are lower than crystalline silicon-based solar cells as the film thickness is kept to a minimal, showing great potential in becoming an alternative to silicon-based solar cells.<sup>2</sup> As promising as they seem, there are major drawbacks such as high toxicity of cadmium and resource scarcity of indium and tellurium. These would hinder the cost as well as sustainability of such cells in the long term. Hence, the primary aim of this project is to search for earth abundant solar absorber materials that are also non-toxic and affordable.

#### **1.4.3** Other emerging solar absorber materials: Perovskites

Apart from those major solar absorber materials mentioned previously, there is a wide range of new and emerging solar absorber materials, of which perovskite materials have gained rising attention especially in the last decade, of becoming a successor to these existing solar absorber materials. Perovskites is the nomenclature for any materials having the same crystal structure as calcium titanate (CaTiO<sub>3</sub>) and in general adopt the chemical formula ABX<sub>3</sub>.<sup>33–36</sup> Until today, there has been record-breaking number of perovskite materials made across the science community. The most com-

mon type of perovskite materials used in solar applications is the organic-inorganic halide perovskites, where cation A is organic and typically consists of methyl or ethylammonium ion and B cation being lead.<sup>35–37</sup> The rising attention in lead halide perovskites has unveiled many attractive properties such as strong optical absorption and low non-radiative recombination rates, however the low melting point, instability to moisture and heat have become some of the biggest challenges in seizing commercialisations of these perovskite solar absorber materials.<sup>38–40</sup> Besides, high toxicity of lead is not ideal and for this reason, other alternative perovskite materials have been continuously investigated.<sup>41</sup> The highest solar cell efficiency in perovskites materials, shown in Figure 1.9, was recorded at 27.3 % with a perovskite-silicon tandem solar cell manufactured by Oxford PV.<sup>42</sup>



Figure 1.9: A graph produced by National Renewable Energy Lab showing the solar cell efficiencies achieved by various research solar cells from 1976 up to 2019.<sup>43</sup>

#### 1.5 Transparent Conducting Oxides

Previously mentioned in section 1.1, the transparent conducting oxide (TCO) layer usually consists of n-type conducting materials and acts as an electrode inside a solar cell which mainly collects electron. TCO materials are known to be both transparent and electrically conducting, therefore it is ideal for TCO materials to have a wide band gap (> 3 eV) and high electrical conductivity in the range of  $1 \times 10^4$  S cm<sup>-1</sup>. In addition, potential TCO candidates should demonstrate high optical transparency across a wide spectrum and low resistivity, and most importantly, they should be highly earth abundant, non-toxic and cheap to make.

The electrical conductivity of a TCO material can be determined by Ohm's law,

$$J=\sigma E$$

where *J* is the current density at a particular point in a resistive material, *E* is the electric field strength at the same particular position and  $\sigma$  quantifies the conductivity.

In Ohm's Law,  $\sigma$  is dependent on the material and hence it can be used to categorize materials into metals, semiconductors and insulators. Metals are highly conductive whereas insulators are not, semiconductors, on the other hand, do not conduct well when they are undoped. Therefore, a lot of research interest has been raised over the years to introduce impurity doping to increase the electrical conductivity. As TCOs are semiconductor materials, doping is necessary to maintain a good level of electrical conductivity, which are dependent on the charge carrier concentration and mobility of the material.

The relationship between charge carrier concentration (*n*), elementary electric charge (*e*), charge carrier mobility ( $\mu$ ) and electrical conductivity ( $\sigma$ ) can be expressed by,

 $\sigma=ne\mu$ 

According to the above equation, increasing charge carrier concentration and mobility can greatly enhance electrical conductivity, however, it is quite often that if a material has a high charge carrier concentration, it will result in a lower charge carrier mobility due to charge carrier scattering. Thus, high electrical conductivity can be achieved with an optimal charge carrier concentration. In general, TCOs are often regarded as degenerate semiconductors, where heavily doped semiconductor materials start to behave like metals. Although it is desirable to achieve a high charge carrier concentration in TCOs, they typically have optimal charge carrier concentration of  $10^{20} \,\mathrm{cm}^{-3}$  in order to remain transparent. While it would be ideal shifting the absorption edges to higher energy, the high charge carrier concentration would lower the carrier mobility and therefore, a balance should be reached. This small shift is known as the Burstein-Moss shift, denoted by  $E_g^{BM}$  in Figure 1.10, it is commonly observed in degenerate semiconductors as electrons start to fill in energy states within the conduction band and moves the Fermi level to a higher energy state. As a consequence, the optical band gap shifts from  $E_g$  to  $E'_g$ .



#### **Burstein-Moss effect**



Burstein-Moss effect can account for the energy shift in band gaps and it is also related to the charge carrier concentration as follow,

$$\Delta E_{BM} = (\frac{h^2}{8m^*})(\frac{3n}{\pi})^{2/3}$$

where  $\Delta E_{BM}$  is the Burstein-Moss shift in energy, *n* is the charge carrier concentration, *h* is Planck's constant and *m*<sup>\*</sup> is the effective mass of an electron.

Thus, the shift induced by Burstein-Moss effect is proportional to the charge carrier concentration of a material.

Since the first appearance of TCO materials such as CdO in the 19<sup>th</sup> century, a wide variety of new materials have been discovered to replace the highly toxic cadmium in the first generation TCO materials, which include ZnO, SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>.<sup>44</sup> These are all n-type semiconductor materials and the most successful TCO material up to this date is tin-doped indium oxide (ITO) due to its low resistivity  $(1 - 2 \times 10^{-4} \,\Omega \,\mathrm{cm})$  and hence a conductivity in the order of magnitude  $\sim 10^4 \,\mathrm{S} \,\mathrm{cm}^{-1}$ , and wide band gap ( $\sim 4 \,\mathrm{eV}$ ). Due to the attractive electrical properties and ease of fabrications, ITO has continued to dominate the commercial market with applications ranging from flat panel displays to thin film photovoltaic devices.<sup>45</sup> Another equally prominent TCO material on the market is fluorine-doped tin oxide (FTO), it is commonly used in opto-electroniccs, touch screen displays, photovoltaics as well as energy-saving windows. Likewise to ITO, doping tin oxide it with F can significantly enhance its electrical conductivity and carrier concentration, resulting in a low resistivity ( $4 \times 10^{-4} \,\Omega \,\mathrm{cm}$ ) and wide band gap ideal for TCO applications.<sup>46</sup>

Despite the success of ITO, the scarcity of In has raised effort to search for other n-type TCO materials with low resistivity and high transparency and ZnO has gained a lot of popularity over the years. ZnO is non conductive and therefore doping it with trivalent ions such as AI and Ga can enhance the electrical conductivity.<sup>47</sup> Introducing electron-rich impurities into an undoped material like ZnO will create a donor energy state

near the conduction band and thus produce electrons as the main charge carriers, resulting in an increase in electrical conductivity. As such, AI and Ga doped ZnO films were found to have band gaps of 3.4 eV and 3.5 eV respectively, than undoped ZnO (3.2 eV), as a result of the high carrier concentration in these doped ZnO films that facilitated the filling of electronic states in the conduction band, which is otherwise known as the Burstein-Moss Shift.<sup>48,49</sup> Particularly, these AI doped ZnO in thin films have resistivity ranging from  $1 \times 10^{-4} \Omega$  cm to as low as  $8.5 \times 10^{-5} \Omega$  cm.<sup>50–55</sup> However, the lowest resistivity can only be obtained at a carrier concentration in the order of  $10^{21}$  cm<sup>-1</sup> and due to the nature of the fabrication process, it would be challenging to commercialise these AI-doped films. Highly transparent Ga doped ZnO films have achieved resistivity ranging from  $1.8 \times 10^{-4} \Omega$  cm to  $2.6 \times 10^{-4} \Omega$  cm.<sup>53,56,57</sup>

Although TCO research has been predominately focused on n-type materials, Hosono et al. reported CuAlO<sub>2</sub> to be the first p-type TCO material back in the late 90s and from then, shown in Figure 1.11, a series of Cu based p-type TCO materials such as SrCu<sub>2</sub>O<sub>2</sub> have been widely investigated.<sup>58–60</sup> Different to n-type TCOs, the impurity atom in this case will have an energy state closer to the valence band and hence producing holes as the majority of charge carriers in the system. Though having a high concentration of holes in the system does not enhance the conductivity due to the immobility of these holes, therefore "Chemical Modulation of the Valence Band (CMVB)" approach is taken into consideration when designing a new p-type TCO material.<sup>61</sup> In CMVB technique, oxides consist of cations with a closed shell such as Ag(I) and Cu(I) have anti-bonding electrons occupying the valence band maximum. Thus having a delafossite structure M<sup>I</sup>M<sup>III</sup>O<sub>2</sub>, where M<sup>I</sup> is either Cu or Ag, M<sup>III</sup> can be trivalent ions such as AI and Ga, can reduce the anti-bonding nature and delocalise the holes at valence band maximum.<sup>62–65</sup> As a result, these p-type Cu-containing TCO materials exhibit a wide band gap above 3 eV and are reasonably conductive, however the conductivity is quite small compared to those of n-type TCOs and it must be significantly enhanced for any future potential TCO applications.



Figure 1.11: A unit cell diagram of  $CuAlO_2$  where Cu atoms, AI atoms and O atoms are shown in blue, lavender and orange respectively.

#### **1.6 Thermoelectric Materials**

In the early 18<sup>th</sup> century, Thomas Johann Seebeck discovered that a circuit composed of two different metal strips, with junctions at various temperatures would deflect a compass magnet. As a young physicist who came from a medical background, Seebeck falsely believed such phenomenon was caused by magnetism induced by temperature difference and related it to the Earth's magnetic field. Years later, it was found that a closed circuit formed and created an electromotive force when two different metal strips were connected. An electric current would also be induced as long as the temperature difference remained in the circuit. This is also known as the Seebeck effect.



Figure 1.12: A diagram illustrating a thermoelectric generator.<sup>66</sup>

A thermoelectric generator is a solid-state semiconductor without any moving parts that can directly convert temperature differences into electricity, employing the Seebeck effect to generate power. There is great potential for thermoelectric devices to become an alternative sustainable energy source as they can recover waste heat generated from household, automotive exhaust and industrial processes and convert it into electricity, recycling energy output and minimizing impacts to the environment. However, it has long been established that present thermoelectric materials are too inefficient to be cost-effective in most applications and since then continuous effort has been made to search for high efficiency thermoelectric materials.<sup>67</sup> As such, what are the desirable properties of a high efficiency thermoelectric material? First of all, the thermoelectric figure of merit (*zT*) must be considered when assessing the useful properties of a thermoelectric material:

$$zT = \frac{\sigma \alpha^2 T}{\kappa}$$

where  $\alpha$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity and  $\kappa$  is the thermal conductivity at temperature *T*.

$$\kappa = \kappa_L + \kappa_e$$

Thermal conductivity  $\kappa$  is composed of two different terms, namely the lattice thermal conductivity  $\kappa_L$  and electronic thermal conductivity  $\kappa_e$ . These terms describe and measure the heat transportation mechanisms within the lattice of a material, the former thermal term originates from phonons travelling through the crystal lattice whereas the thermal electronic conductivity is governed by the charge carriers transporting heat in the lattice. The electronic thermal conductivity can be associated with conductivity via the Wiedemann-Franz law, which is shown as:

$$\kappa_e = L\sigma T$$

where *L* is the Lorentz number,  $\sigma$  is the electrical conductivity and *T* is the temperature in Kelvin.

Power factor is another term frequently used in assessing the suitability of a thermoelectric material and it is correlated to the electrical conductivity  $\sigma$  and Seebeck coefficient  $\alpha$  as follows:

 $PowerFactor = \sigma \alpha^2$ 

Although having a large  $\alpha$ ,  $\sigma$  and small  $\kappa$  at temperature T are desirable to achieve the optimal zT, which is required for ideal thermoelectric materials, low carrier concentration insulators and semiconductors often have large  $\alpha$  but suffer from low  $\sigma$ . As shown in Figure 1.13, increasing the carrier concentration will achieve a higher  $\sigma$  as well as  $\kappa$ , hence it is often a compromise between large thermopower (absolute value of  $\alpha$ ) and high  $\sigma$ .<sup>68,69</sup> Subsequently, the power factor is only a thermoelectric property of a material and will always remain as a compromise between  $\alpha$  and  $\sigma$ . Second of all, it is important to achieve a balance between the effective mass and mobility of the dominant charge carriers as large effective masses can increase the Seebeck coefficient but suffer from low electrical conductivity and hence low mobility.<sup>70</sup> Last but not least, thermal conductivity can be catergorized into electronic and lattice thermal conductivity ( $\kappa_e$  and  $\kappa L$  respectively), ideal thermoelectric materials should have a minimal lattice thermal conductivity and reasonably high mobility in order to effectively scatter lattice phonons, and maintain a high electrical conductivity.<sup>71</sup> These prominent materials are also known as 'phonon-glass electron-crystal' (PGEC) materials, which usually contain heavy atoms at partially filled sites in the structure, such that they behave like glass or amorphous material and thus have low lattice thermal conductivity while they also have high electrical conductivity similar to that in a crystal.<sup>72-74</sup>



Figure 1.13: A graph showing the correlation between zT and different parameters at various carrier concentrations.<sup>71</sup>

First generation thermoelectric materials such as PbTe and Bi<sub>2</sub>Te<sub>3</sub> are still the most commonly used materials today due to their high *zT* values of about 1 up to  $200 \circ \circ$ C. Both materials can be alloyed with PbSe and Bi<sub>2</sub>Se<sub>3</sub> respectively to form p-type PbTe<sub>1-*x*</sub>Se<sub>*x*</sub> and n-type Bi<sub>2</sub>Te<sub>3-*x*</sub>Se<sub>*x*</sub>.<sup>69</sup> The limitation of working temperature has encouraged the specific application of thermoelectric materials as well as the use of multiple thermoelectric material segments in assembly of a thermoelectric device.<sup>75,76</sup> It was later discovered that the fine tuning of carrier concentration of a material can further reduce the lattice thermal conductivity and thus achieve even higher zT values. Most of these alloys contain Sb, Bi, Te and Se, the typical values of zT range from 0.8 to 1.1 depending on the carrier concentration. These alloys can also be optimised to work at different temperatures, enabling a wide range of applications. Due to high toxicity and resource scarcity of these Te and Pb-containing alloys thermoelectric materials, the search for better alternative materials has heightened throughout the decades, the basic requirements for these alternative thermoelectric materials include high earth abundancy, non-toxicity, narrow band gaps. In addition, it is also important to incorporate
high zT (zT>1) values, low lattice thermal conductivity and high carrier concentration in designing new thermoelectric materials.

Regardless of the different ways and methods to modify properties of a thermoelectric material, the ultimate goal is to enhance the *zT* value. Nanostructuring is one of the predominant methods to enhance zT through altering the thermal properties of a material, particularly the lattice thermal conductivity can be significantly reduced.<sup>77–81</sup> Phonons are quantised lattice vibrations present in a lattice, they often carry energy in the form of heat within the lattice. Various phonon scattering processes limit the thermal transport properties within a lattice and since the thermal transport property is dependent on the mean free path, which is the furthest distance phonons can travel before being scattered, elongating the mean free path of phonons can effectively reduce the scattering process and therefore reduce the lattice thermal conductivity. This elongation of the mean free path can be achieved with nanostructured and multi-layered super-lattices within a thermoelectric material as it increases scattering of phonons between the layers and reduces the thermal conductivity. In addition, Seebeck coefficient will also be enhanced due to quantum confinement effect where the particle size is so small that it is now comparable to mean free path and wavelength of electrons, which increases the density of states within the electronic structure of the material.

In contrast to the Seebeck effect, the thermoelectric cooling effect, which is also known as Peltier cooling effect, occurs when electricity is being supplied to the device and converted into heat energy instead. The generated heat energy is then used to establish a temperature gradient in a thermocouple device and acts as a cooling device.

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# Chapter 2

# **Characterisation Methodology**

## 2.1 Powder X-ray Diffraction



Figure 2.1: A schematic diagram illustrating X-ray diffraction and Bragg's Law.

In X-ray diffraction, X-rays beams are generated and scattered by atoms in periodic arrays with long range order when they irradiate upon a crystal sample. These periodic arrays are also known as Miller planes. Since the layer of atoms are ordered and arranged repeatedly in these Miller planes, and the interatomic and interplanar distances between atoms and layers in a crystal structure are of the order of 0.1 nm, only X-rays within the suitable wavelength range of 0.1 nm to 10 nm can interact with the atoms in a material. Thus, these X-rays are being diffracted by each plane. The angle

at which the incident X-ray is being diffracted is known as  $\theta$  with respect to the miller planes. When incident X-ray is diffracted by the Miller planes, and the path difference between diffracted X-rays is an integer of the X-ray wavelength  $\lambda$ , constructive interference occurs, which will result in a signal at the detector, thus allowing the formation of a diffraction peak. On the other hand, diffraction peak will not form if destructive interference occurs, in which the path difference is not an integer of the X-ray wavelength  $\lambda$ . The overall diffraction process can be related and represented by Bragg's Law as follow,

In Figure 2.1, the diffraction angle  $\theta$  can be expressed as

$$sin\theta = \frac{AB}{d}$$

Rearranging the equation gives

$$AB = dsin\theta$$

Because the path difference is equivalent to the total distance of AB and BC and AB = BC,

$$2AB = 2dsin\theta$$

As mentioned previously, a diffraction peak is present only when there is constructive interference, which *2AB* must be an integer multiple of the incident X-ray wavelength and thus Bragg's law is derived as follow,

$$2dsin\theta = n\lambda$$

where *n* is an integer,  $\lambda$  is the X-ray wavelength,  $\theta$  is incident angle of the X-ray and *d* is the spacing between atomic layers.

Powder X-ray diffraction is incredibly useful in identifying and distinguishing between different phases of as-synthesised powder materials.

As d<sub>hkl</sub> is a function of the size and shape of crystal lattice, the diffraction peak position is a product of the average atomic distances in the crystal. The structure factor quantifies the amplitude of light scattered by a crystal, which is dependent on the atomic arrangement in the Miller planes. Both factors affect the positions of the diffraction peaks whereas the absolute intensities of diffraction peaks can vary due to instrumental and experimental parameters, namely atomic coordinates, temperature and site occupancies. The positions, intensities and shapes of diffraction peaks are essential information required in post-PXRD analysis such as Rietveld refinement.

#### 2.1.1 Characterization

All powder X-ray diffraction (PXRD) data was collected on a STOE diffractometer in transmission geometry using monochromated Mo K $\alpha$  radiation over the 2 $\theta$  range of 2° to 40° with a step size of 0.5° at 20 s per step.

#### 2.1.2 Rietveld Refinement

Since a crystal structure describes the atomic arrangement of a material and the unit cell is a basic repeating unit that defines such crystal structure, Rietveld refinement can be performed to identify phases and extract useful information such as lattice parameters and bond lengths. Once an X-ray diffraction pattern is obtained, it can be used in conjunction with software such as GSAS/GSAS II to carry out Rietveld refinement process. During each refinement cycle, the programme will generate a best fit of diffraction pattern to the experimental diffraction pattern based on the input crystal structure data. Different parameters can be refined individually in order to improve the calculated diffraction pattern. These parameters are usually concerned with the peak shape, intensity and position, which are dependent on both the instrumental and experimental conditions. Peak shape in particular is mostly affected by instrumental conditions, for example the calculated peak shape can be improved upon multiple re-

finement cycles by refining the Gaussian and Lorentz parameters. As the refinement continues, a close fit between the calculated and experimental diffraction patterns will be obtained which a refined lattice parameters can also be extracted. R-factors such as the weighted profile R factor,  $R_w$  is often used to determine the fit between calculated and experimental diffraction patterns. Another value that can determine the fit is the chi square  $\chi^2$  value, it is also known as the Goodness of Fit where it decreases with an increasingly good model. Despite these values often being used in quantifying the fit between the calculated and experimental models, they may not provide an accurate representation of the fit as they can be heavily deflected by factors such as a noisy baseline in the diffraction pattern. Thus, a good fit between the calculated and experimental patterns can simply be determined by the user.<sup>82</sup>

Rietveld refinement is often used to confirm the phase purity and calculate the lattice parameters of a material, especially in identifying as-synthesized powder materials. This will enable a more detailed outlook into the crystal structure and atomic arrangement of as-synthesised undoped and doped materials presented in this thesis.

## 2.2 Ultraviolet-Visible Spectroscopy

Optical Diffuse-Reflectance spectroscopy is used in conjunction with Ultraviolet-Visible (UV-Vis) spectroscopy to obtain the optical band gaps of all the as-synthesised powder materials. Light source with a wavelength between 10 nm and 2500 nm is applied in UV-Vis spectroscopy to obtain useful information in the optical structure of a material. A typical UV-Vis spectrometer set-up involves a deuterium/tungsten dual lamp, covering the range of wavelength of light required to run the measurement. Depending on the selected choice of wavelength range, the light source will be filtered according to their wavelength once it has passed through a monochromator and only light of the selected wavelength range will be utilised in the measurement. UV-Vis spectroscopy is widely used in the physical sciences as it has the ability to measure the optics of materials in three different modes, either in absorbance, transmittance or reflectance, in which the differences between each mode can be found in Chapter 1.2.

In Diffuse-Reflectance spectroscopy, measurements can be carried out with the use of integrating spheres inside the UV spectrometer. The integrating spheres allow part of the incident light beam to reflect in all directions where some of the light beams will also be refracted and scattered inside the sample. The intensity of scattered light collected is independent of the angle of incidence.

#### 2.2.1 Tauc Method

Diffuse-Reflectance measurements for all as-synthesised powder samples were transformed using Kubelka-Munk function, where F(R), which is considered to be proportional to absorption assuming that the scattering is constant throughout the wavelength range used in the measurement.<sup>83,84</sup> Tauc Method was first introduced to determine the band gap of amorphous semiconductor materials, such as amorphous silicon and one of the fundamental underlying assumptions validating Tauc method stated that momentum is not conserved in the optical transitions. As a result, forbidden optical transitions can also be accounted for while determining the band gap of a semiconductor material. Due to the inhomogeneities of powder materials, Kubelka-Munk function provides a good approximation in transforming the Diffuse-Reflectance data into values proportional to absorption. In order for Kubelka-Munk function to be valid, the powder sample is assumed to be densely packed together and have a rough surface to facilitate the diffuse reflected light. Moreover, the size of powder is also assumed to be comparable to that of the wavelength of light to reduce specular reflected light, which often occurs at the surface of powder sample.

Raw reflectance data collected in % reflectance ( $R_{data}$ ), from UV-Vis spectroscopy, will first be transformed into the absolute reflectivity values ( $R_{absolute}$ ),

$$R_{absolute} = \frac{\% R_{data}}{100}$$

Kubelka-Munk function is shown as follow:

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{K}{S}$$

where  $R_{\infty}$  is the powder with infinite thickness, K is the absorption coefficient and S is the scattering coefficient. All band gap values determined using Tauc method are assumed to be direct allowed optical transitions.

Values of F(R) and Tauc are obtained and plotted against photon energy, the optical band gap can be extrapolated from the linear region of absorption in the Tauc plot, at which y=0. Despite the Tauc method being widely used to determine optical band gap in both amorphous and polycrystalline semiconductor materials, it was originally proposed for use in amorphous semiconductor materials. A further investigation into the accuracy of using Tauc method in polycrystalline materials have proved that it is reasonably accurate to obtain the optical band gap of such materials.<sup>85</sup>

#### 2.2.2 Poeppelmeier Method

Poeppelmeier and his team have proposed a method for accurate determination of the band gap in crystalline and degenerate semiconductors, the major difference between Poeppelmeier and Tauc method is that Poeppelmeier takes into account the presence of a large concentration of charge carriers in crystalline materials whereas Tauc method was originally used to assess amorphous materials.<sup>86</sup> Therefore, Poeppelmeier method is adopted to determine the optical band gaps in some of the assynthesised materials as opposed to Tauc method. In Poeppelmeier method, diffuse-reflectance measurements are first transformed using Kubelka-Munk function to obtain the plot of F(R) against photon energy, value of E<sub>1</sub> can be extrapolated from the linear region of the absorption in the plot. These transformed data are converted into  $F(R)^2$ , a second plot is generated where the second value E<sub>2</sub> can be obtained.

Optical band gap  $E_g$  can be calculated using the Poeppelmeier equation,

$$E_q = 2E_2 - E_1$$

As there is no indication or validity in current research on whether Poeppelmeier method can be used in non-degenerately doped semiconductors, it is a good alternative to Tauc method to assess the band gaps in these materials. Some optical band gaps of the as-synthesised materials are determined via Poeppelmeier method and the values are evaluated together with Tauc method and compared against theoretical results.

#### 2.2.3 Characterization

Optical diffuse-reflectance spectroscopy was measured between 205 nm to 2000 nm with a step size of 1 nm using PerkinElmer Lambda 950 UV-vis spectrophotometer equipped with an integrating sphere at ambient temperature.

## 2.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique to determine the elemental composition, chemical state and electronic state of the surface of a material. In XPS, a beam of X-rays with typically 1.486 kV of energy are utilised in a high vacuum environment and irradiate upon the surface of a sample material. The surface depth of a material at which it is sensitive to XPS measures from 1 nm to 5 nm, beyond which is considered as the bulk of a material. The surface depth of a material is strictly limited because the likelihood of inelastic collisions of electrons increases with the depth of a material, making it more difficult for photoemission to occur.<sup>87</sup> Having a specific surface depth also allows electrons to be emitted from the top layer efficiently, the kinetic energy of these electrons are being measured at the detector.

The overall photoemission process is shown below.



Figure 2.2: A diagram illustrating the photoemission process involved in XPS surface analysis.

Since the kinetic energy (KE) of these electrons are dependent upon the irradiated photon energy (*hv*), binding energy (BE) of the electron and the work function of the sample ( $\phi_{\text{sample}}$ ), which is considered to be the energy required for an electron to escape the Fermi level into the vacuum. The overall equation that governs the photoemission process can be described as:

$$KE = hv - (BE + \phi_{sample})$$

However, the work function of the spectrometer should also taken into consideration in the photoemission process, it acts as an adjustable instrumental correction during the process and is often a constant value. To include the work function of the spectrometer, the equation is now:

$$KE = hv - BE - \phi_{sample} - (\phi_{spectrometer} - \phi_{sample})$$

which essentially gives,

$$KE = hv - BE - \phi_{spectrometer}$$

Rearranging the equation gives,

$$BE = hv - KE - \phi_{spectrometer}$$

The binding energy at which a peak is located in a XPS spectrum will show the information necessary to determine the oxidation state and chemical environment of a constituent elemental species, this is done by measuring the kinetic energy emitted during the process due to different electrons requiring different energies to escape their orbitals. In additional, XPS is also very useful in identifying contaminants on the surface of a material as well as probing into the valence band of a material.

In most XPS spectra, multiple peaks are present at core levels due to spin orbit splitting and therefore it is important to understand how spin orbit splitting affects the appearances of peaks.

Considering the *j*-*j* coupling rule,

j = l + s

where *s* is the spin angular momentum number  $(\pm \frac{1}{2})$  and *l* is the angular momentum quantum number. All orbital levels will give rise to a doublet except *s* levels with *l* being 0. XPS peak and peak area corresponding to a doublet will differ in binding energies with respect to the degeneracy of each spin state.<sup>88,89</sup> It is notably important to include the spin orbit splitting effect whilst analysing XPS data.

Table 2.1: The respective subshells and their corresponding l, j values and peak area ratios.

Subshell	1	j	Area Ratio
S	0	$\frac{1}{2}$	-
p	1	$\frac{1}{2} / \frac{3}{2}$	1:2
d	2	$\frac{3}{2} / \frac{5}{2}$	2:3
f	3	$\frac{5}{2} / \frac{7}{2}$	3:4

#### 2.3.1 Characterization

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scentific K $\alpha$  spectrometer utilizing a 72 W Al K $\alpha$  radiation. High resolution scans with a binding energy step size of 0.1 eV was used and in situ Ar ion etching was performed using a 2 keV Ar ion beam in a background Ar pressure of  $2 \times 10^{-7}$  mbar. The binding energy scale was corrected for charging by adjusting the adventitious C 1*s* peak to 284.8 eV.

### 2.4 X-ray Fluorescence

X-ray Fluorescence (XRF) describes the emission of characteristic X-rays from the sample. Short wavelength X-ray sources are utilised to excite an electron in an inner shell of an atom within the sample, causing the electron to be ejected from its shell while creating an electron hole. An electron from a higher energy shell will fill the hole, and release energy in form of a photon that is also equivalent to the difference in energy between the higher energy shell and lower energy shell. This process yields a fluorescent photon with a characteristic energy and the energy released is measured by the detector in XRF spectrometer.<sup>90</sup> The wavelength or energy can be calculated via the Planck-Einstein relation, which is shown below.<sup>91</sup>

$$\lambda = \frac{hc}{E}$$

XRF is a non-invasive technique to determine the elemental bulk composition of a

material and it is particularly useful for powder samples, specifically novel materials. As XRF is carried out in air at ambient temperature, it provides a quick and reliable way to obtain material composition information.

#### 2.4.1 Characterization

Samples were measured using Malvern Panalytical Epsilon 1 XRF analyzer equipped with an 50 kV Ag anode X-ray tube. Samples, in form of powder, were placed in the sample holder and transferred to the detection chamber for analysis. All measurements were run in ambient air environment.

### 2.5 Energy Dispersive Spectroscopy

In Energy Dispersive Spectroscopy (EDS), the spectrometer is typically equipped and run with a scanning electron microscopy (SEM) machine, which provides a beam of high energy electrons for exciting a ground state electron from an inner shell, causing the electron to be ejected and leaving an electron hole in the original shell. An electron from a higher energy shell fills the hole and energy is released during this movement of electron from a higher energy shell to a lower energy shell. The energy difference is usually released in the form of an X-ray. An EDS spectrometer is equipped with a detector to measure the relative abundance and energy of X-rays emitted from a sample to detect the number and energy of photons emitted from the sample. Since the emitted X-rays are unique and characteristic between different energy shells of an element, this allows multiple elemental bulk compositions of a sample to be measured instantly.<sup>92-94</sup>

#### 2.5.1 Characterization

All EDS measurements were conducted using a Philips XL30 ESEM and a JEOL JXA-8600 superprobe. EDX measurements were carried out using an acceleration voltage of 20 kV, magnification of 500 and acquisition live time of 60 seconds under high vacuum. All powder samples were coated with a thin layer of carbon to enhance conductivity.

## 2.6 Hall-effect

Hall-effect four-point probe is usually used to measure the resistivity of a sample given that the following criteria are satisfied: all four-point contacts are small and at the boundary, the sample is uniformly doped and uniformly thick and there are no holes in the sample. A measurement is carried out by allowing a current to pass between two contacts A&B while the induced Hall voltage is measured between two other different contacts C&D. This can eliminate the contact resistance in the measurement. Introducing a magnetic field near the sample during the measurement will disrupt the flow of charge carriers due to the induced Lorentz Force, causing electrons and holes to migrate towards opposite ends in the sample, thus inducing a voltage called the Hall voltage across the sample. Hall-effect measurements can also yield the quantity of the majority carrier density in a sample.

Resistivity, mobility and density of major charge carriers of a material can be found in Hall-effect measurements and hence the type of doping can also be determined. Despite the relatively simple and straightforward operation of Hall-effect four-point probe, it is a invasive characterisation technique and has a number of limitations including the significant dependence upon the sample thickness, the homogeneity of the sample and the grain size of the sample.

### 2.6.1 Characterization

Conductivity measurements were attempted on most of the as-synthesised samples using an Ecopia HMS-3000 instrument and a Van der Pauw electrode geometry.

## 2.7 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is used to measure the change in mass of a sample with the change in temperature over a specific period of time. A TGA machine is equipped with a precision balance and a furnace, the temperature of furnace is controlled by a programme and increases at constant rate to start a thermal reaction between the sample and air or other inert atmospheres. The change in mass will be recorded simultaneously as the temperature increases, hence, the mass loss and phase change of a sample can be detected over a specific time scale. TGA is a convenient tool to investigate the decomposition temperature and process of a material.

#### 2.7.1 Characterization

TGA was measured on NETZSCH STA 449 TGA analyzer, measurements were recorded from room temperature 20 °C to 1000 °C in air.

## 2.8 Terahertz Spectroscopy

Terahertz time-domain spectroscopy (THz-TDS) is a technique measuring the conductivity of metals, semiconductors, 2D materials and biological proteins. In materials science, THz-TDS is widely used to measure the charge carriers in a material since they reflect and absorb THz radiation. In THz-TDS spectroscopy, optical pulses generated by the ultrafast laser oscillator are transformed into a picosecond THz pulse which are used for measurement. The ultrafast laser will also generate another optical pulse for detection purposes. By scanning the delay line between the two pulses, the amplitude of the THz signals can be collected as a function of time. These will be converted via Fast Fourier transformation (FFT) in order to obtain the intensity of the THz signal as a function of frequency.<sup>95</sup>

#### 2.8.1 THz-TDS data processing

Information such as the frequency-resolved amplitude and phase of an electromagnetic wave can be obtained through THz-TDS. As such, an air measurement is often used as a reference in each measurement cycle to determine the changes in phase as well as amplitude simultaneously. Each cycle measures a Teflon-mixed sample, Teflon and air. Note that all of these quantities are complex-valued.

In short, the complex refractive index of the sample can be calculated by:

$$\frac{E_{sample}}{E_{reference}} = T = \tau_{0p} P_p \tau_{p0}$$

where the subscripts 0 and p denote the two different mediums, and  $P_p$  is the propagation operator, often described as:

$$P_p = e^{-ik_0 d(n_p - 1)}$$

The changes in absorption and phase of an electromagnetic wave propagating through a medium with thickness d and complex refractive index of  $n_p$  can be described by the propagation operator.

And the Fresnel coefficient ( $\tau_{ij}$ ) for an electromagnetic wave entering medium *p* coming from medium *0* is shown as follows,

$$\tau_{0p} = \frac{2n_0}{n_0 + n_p}$$

where  $n_0$  and  $n_p$  are the refractive indices for medium 0 and p respectively.

Effective medium theory (EMT) was used to calculate the refractive index and establish a relationship between the refractive index and permittivity of the sample. Refractive index obtained via THz-TDS consists of a real and an imaginary part.<sup>96,97</sup> EMT also allows a correlation between the complex permittivity values of Teflon and the sample:

$$V_T \frac{\varepsilon_T - \varepsilon_p}{\varepsilon_T + 2\varepsilon_p} + V_s \frac{\varepsilon_s - \varepsilon_p}{\varepsilon_s + 2\varepsilon_p}$$

where T and S denote Teflon and the sample respectively and p represents the measured permittivity value.

The equation can then be solved with known volume fractions of Teflon and the sample,  $V_T$  and  $V_S$  respectively. The complex permittivity values can also be used to obtain the absorption coefficients by calculating the complex refractive index:

$$n_s = \sqrt{\varepsilon_s}$$

and

$$\alpha = 2n_s^{"}k_0$$

where  $k_0$  is the wavevector in vacuum.

All of these complex-valued data were numerically solved using built-in equations and the optimization tool box in a MATLAB code developed by Prof. Charles Schmuttenmaer's Group at Yale University USA.

#### 2.8.2 Characterization



Figure 2.3: A schematic diagram showing an experimental set-up of a THz-TDS system.<sup>95</sup>

The spectrometer was equipped with a Titanium Sapphire laser as the main source of ultrafast optical (50 fs) pulses with a central wavelength of 800 nm. THz pulse generated had a bandwidth of 0.3 THz to 3 THz. The laser beam was split equally, it was partially used for the THz light generation with an interdigitated photoconductive GaAs antenna and the other half of the beam, the near-IR pulse, was directed to an identical photoconductive antenna for THz detection. In the time domain window, the electric field of the pulse was recorded. The purge-box was filled with dry nitrogen in order to minimise the absorption of THz beam by atmospheric water vapour.<sup>96,97</sup>

 $GaSbO_4:ZnSb_2O_6$  powder samples were ball-milled for 900 s and mixed with Teflon in a approximate ratio of 0.025 g to 1.030 g. All mixtures were then pressed into pellets with a hydraulic press, these pellets were all 13 mm in diameter and roughly 3 mm thick. Two sample-Teflon pellets and a pure Teflon pellet were transferred and mounted onto a sample plate inside the purge box. During each measurement cycle, data were recorded from the sample-Teflon pellet, Teflon pellet and air respectively. In order to ensure that the measured transmission is independent of the spectral bandwidth, intensity and dynamic range, an air measurement was in place to eliminate the influence

of the THz spectrometer. In addition, pure Teflon pellet was used as a reference due to its negligible absorption in the THz range and chemical inertness, thus reducing the THz absorption by the sample-Teflon pellets. All pellets were measured and recorded over the temperature range of 300 K to 65 K in steps of 50 K with the use of a liquid nitrogen sample-in-vapour and low pressure cryostat.

%  Ga	Sample Mass	Teflon Mass	
	(g)	(g)	
0 %	0.026	1.031	
2%	0.025	1.020	
8 %	0.026	1.017	
10%	0.026	1.024	
15%	0.025	1.019	
20%	0.026	1.021	
100%	0.025	1.018	

Table 2.2: Sample to Teflon ratios in all pellets measured in THz-TDS experiment.

#### 2.9 Seebeck Measurements

Thermoelectric properties can be determined by carrying out Seebeck measurements and derived through the equation shown below:

$$zT = \frac{\sigma \alpha^2 T}{\kappa}$$

where  $\alpha$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity and  $\kappa$  is the thermal conductivity at temperature *T*.

All of these thermoelectric quantities can be measured simultaneously using a designated instrument. A detailed introduction on thermoelectrics can be found in the Chapter 1.6.

### 2.9.1 Characterization

Simultaneous electronic conductivity ( $\sigma$ ) and Seebeck coefficient (S) measurements were made on an Ulvac-Riko ZEM-3 instrument from rectangular bars (dimensions of 2 × 2 × 8 mm) which were cut from sintered pellets using a low-speed diamond-blade saw. The bars were mounted in a 4-point geometry with outer current electrodes in contact with each end face and inner thermocouple and voltage probes pressed against one of the longer (8 mm) sides of the bar. The sample chamber was evacuated and purged three times with helium and then dosed with 0.01 MPa of helium before commencing measurement. Data were recorded at 50 K intervals from 323 K to 973 K, applying 10, 20 and 30 K temperature gradients to the bar at each temperature step. Errors on both  $\sigma$  and S were assumed to be 5% on advice of the manufacturer.

# **Chapter 3**

# NaSbS<sub>2</sub>

### 3.1 Solar Absorber Material



Figure 3.1: (a) Unit cell structure of  $NaSbS_2$  and (b) structure of  $NaSbS_2$  viewed along (010). Na atoms are green, Sb atoms are pink and S are yellow in colour. The unit cell boundary is marked in black and only short Sb-S bonds are displayed.

Many of the ternary antimony chalcogenides including CuSbS<sub>2</sub> have gained rising attention in the last five years due to their non-toxicity, high earth abundancy and strong optical absorption, which are all suitable properties for a new sustainable material for thin film solar cells. CuSbS<sub>2</sub> thin films have been previously reported by various computational and experimental publications to have band gaps between 1.4 eV to 1.6 eV, <sup>98–101</sup> and a noticeably high initial solar conversion efficiency of 0.5 % to 3 % was achieved with different prototypes of CuSbS<sub>2</sub> thin film solar cells. <sup>101–104</sup> Other related

ternary semiconductors are mostly  $Ag_x(Bi/Sb)_ySe_z$  or  $Ag_x(Bi/Sb)_yTe_z$  materials, where the compositions x, y and z of these compounds can be easily altered to optimise the structural and electronic properties. In addition, these ternary semiconductor materials have displayed yet another ideal property– strong absorption coefficients, and hence they have attracted an ongoing interest in photovoltaic applications.<sup>105–107</sup> Are there other antimony chalcogenides that could possess similar properties given such prior success with ternary antimony semiconductors and would it become an even better alternative solar absorber material?

Most recently, quantum dot-sensitized solar cells (QDSSCs) displaying a relatively high solar efficiency of 2.22 % have been made with NaSbSe<sub>2</sub> nanocrystals.<sup>108</sup> On the other hand, NaSbS<sub>2</sub> as a sister compound of NaSbSe<sub>2</sub>, although being less explored as a solar absorber material, has also shown a few promising features of becoming an efficient photovoltaic material. Having an experimental band gap value of 1.5 eV to  $1.8\,\mathrm{eV}$  and a large absorption coefficient  $\sim 10^4\,\mathrm{cm^{-1}}$  to  $10^5\,\mathrm{cm^{-1}}$  within the visible light region.<sup>109–111</sup> NaSbS<sub>2</sub> seems to be a very attractive candidate. Furthermore, Rahayu et al. have also demonstrated a strong absorption of light in NaSbS<sub>2</sub> coated semiconductor-sensitized solar cells, with the photovoltaic efficiency of this SSC increased from 2.30 % to 3.18 % under reduced light intensity.<sup>110</sup> In addition, another research led by Sun et al. have assembled NaSbS<sub>2</sub> quantum dot-sensitized solar cells and they were shown to have an efficiency as high as 4.11%, which is a remarkable efficiency to date.<sup>112</sup> Recent theoretical calculations of NaSbS<sub>2</sub>, using a Modified Becke-Johnson (MBJ) exchange potential, have shown a band gap of 1.21 eV and that this material could potentially be defect tolerant, as suggested by the strong indication of hybridization between S p and Sb s states.<sup>113</sup>

In this chapter, we will elaborate on our interest in NaSbS<sub>2</sub> by experimentally examining the optical and structural properties of solid-state synthesized NaSbS<sub>2</sub> powder using a wide range of characterisation techniques including Powder X-ray Diffraction (PXRD), UV-Vis spectroscopy (UV-Vis), X-ray Photoelectron Spectroscopy (XPS). These experimental results will be compared and explained together with the theoretical model

generated by hybrid Density Functional Theory as a collaboration with the Scanlon Materials Theory Group (STMG).

## 3.2 Experimental Methodology

 $Na_2S \cdot 9 H_2O$  ( $\geq 98 \%$ , Sigma-Aldrich) was first dessicated under dynamic vacuum at 200 °C for a minimum of 2 days to obtain anhydrous  $Na_2S$ . 0.2201 g of dehydrated  $Na_2S$  and 0.9610 g of  $Sb_2S_3$  ( $\geq 96 \%$ , Inoxia) were ground together in an agate mortar and pestle. The stoichiometric mixture was carefully transferred to a quartz ampoule and heated under dynamic vacuum at 550 C for 2 h, with heating and cooling rates of  $5 \,^{\circ}C \,^{min^{-1}}$ .

 $Na_2S + Sb_2S_3 \longrightarrow 2NaSbS_2$ 

## 3.3 Results and Discussion



Figure 3.2: Experimental powder X-ray diffraction pattern of NaSbS<sub>2</sub> and refined pattern are shown with the difference between the experimental and calculated intensities in black. Pure phase is indicated as pink.

Figure 3.1 shows the structure of NaSbS<sub>2</sub>, it is monoclinic and consists of [4+2] Sb-S chains, with 4 longer Sb-S chains and 2 shorter Sb-S chains. Sodium atoms are sitting in a distorted octahedral environment. Rietveld refinement was carried out using a structural model in the C2/c space group and it is refined against the experimental

PXRD data using GSAS and EXPGUI software. During the refinement process, parameters concerning the peak shape and unit cell were refined until a goodness of fit value of 3.8 was obtained. As-synthesised NaSbS<sub>2</sub> powders are phase pure as clearly indicated in Figure 3.2, where the experimental and calculated powder X-ray diffraction pattern from Rietveld refinement of NaSbS<sub>2</sub> are also displayed.<sup>114</sup> No additional phases were detected.

	Experimental NaSbS <sub>2</sub>	Literature NaSbS <sub>2</sub> <sup>114</sup>	
	(Å)	(Å)	
a	8.249(1)	8.232(1)	
b	8.278(1)	8.252(2)	
c	6.851(1)	6.836(1)	
β	124.25(1)	124.28(1)	

Table 3.1: Experimental and literature lattice parameter values of NaSbS<sub>2</sub>.

Lattice parameters and volumes of the experimental structure were obtained from Rietveld refinement and are in good agreement with the observed NaSbS<sub>2</sub> structure, which are shown in Table 3.1.

Table 3.2: Ca	alculated I	lattice parar	neters of N	VaSbS <sub>2</sub> , v	with percenta	age differe	ences from
experimental	results						

	HSE06	% difference from			
	(Å)/°	As-synthesised $NaSbS_2$	Fourcade et al. <sup>115</sup>		
a	8.2612	+0.15	+0.35		
b	8.3931	+1.39	+1.71		
С	6.8209	-0.43	-0.22		
$\beta$	124.15	-0.08	-0.10		

As a result of the computational relaxation, the equilibrium lattice parameters of structurally relaxed NaSbS<sub>2</sub> are included in Table 3.2. There is only very slight (<1.5 %) expansion in a and b lattice parameters, and contraction in c similar to the as-synthesised NaSbS<sub>2</sub> sample and a similar deviation is also exhibited from the Fourcade structure.



Figure 3.3: X-ray photoelectron Spectra of (a) Na 1*s*, (b) Sb 3*d* with overlapping O 1s regions are shown.



Figure 3.4: X-ray photoelectron Spectra of (a) S 2*p* and (b) experimental valence band data overlaying with simulated valence band data taken from calculated DOS for NaSbS<sub>2</sub> with a smear value of 0.47, both recorded up to -15 eV.

Photoemission spectra of NaSbS<sub>2</sub> shown in Figure 3.3 and Figure 3.4 are analysed with curve fitting. A Shirley function was used to model the background while a convolution of Gaussian and Lorentzian functions in ratio of 70:30 were applied to model the spectral components. These components were constrained according to the expected intensity (area under the peak) ratios and splitting constants for spin orbit doublets whenever necessary. The as-synthesized NaSbS<sub>2</sub> powder sample was etched for 10 min, using a 2 keV Ar ion beam, to significantly reduce the amount of oxygen contaminant on the surface. A symmetrical Na 1s peak at 1071.5 eV corresponding to Na(I) can be observed in the high resolution scan in Figure 3.3.<sup>116</sup> The same figure also shows that the Sb 3d spectra consists of a spin-orbit doublet, where there is a higher binding energy component Sb  $3d_{3/2}$  at 539.8 eV and lower binding energy component Sb  $3d_{5/2}$ , at 530.4 eV.<sup>117,118</sup> There is overlapping between the O 1*s* peak and lower energy component Sb  $3d_{5/2}$ . For the reason that Sb (III) and Sb (V) species are indistinguishable on the surface, it is possible that both species co-exist on the surface.<sup>119</sup> However, the presence of Sb (V) in the as-synthesized NaSbS<sub>2</sub> powder would have caused the unit cell lattice to shrink due to it having a smaller ionic radius (0.60 Å) than Sb (III) (0.76 Å), yet the refined experimental lattice parameters shown previously suggested that Sb (III) are the only species present in the bulk of as-synthesized NaSbS<sub>2</sub> powder.<sup>120</sup> The significantly reduced amount of oxygen contaminant on the surface post etching can be accounted for the small trace shoulder region visible in the Sb  $3d_{5/2}$  component of the sample. A much larger shoulder region corresponding to the same oxygen species was observed in the same region of the non-etched NaSbS<sub>2</sub> sample otherwise. In Figure 3.4, S 2p spectrum shown was composed of an overlapping spin-orbit doublet, the lower binding energy component S  $2p_{3/2}$  peak at 162.2 eV is consistent with expectations for S<sup>2-</sup> ions, whereas the higher binding energy component corresponding to sulphate species was not observed after etching, indicating the likelihood that some of the sulphides were partially oxidised on the surface and turned into sulphates. 121-123



Figure 3.5: Electronic Density of States of NaSbS<sub>2</sub>, calculated using HSE06+SOC; E = 0 is set to the valence band maximum.

Figure 3.5 shows the electronic Density of States (DOS) of NaSbS<sub>2</sub>. Although NaSbS<sub>2</sub> is structurally very similar to a rock salt structure, the C2/c ground state can be seen as a distorted octahedral (rock salt) cation environment with a [4+2] Sb environment due to the active lone pair occupying part of the coordination sphere. The conduction band of NaSbS<sub>2</sub> in further accordance with the model is dominated by the Sb p and S p states, this observation is native to many lone pair materials, for example, the stoichiometric counterpart of NaSbS<sub>2</sub>, CuSbS<sub>2</sub>. Photoionisation cross-sections were scaled accordingly in the density of states output and smeared appropriately to reproduce the broadening effect observed experimentally. As a result, the density of states matches well to our valence band XPS spectrum displayed in Figure 3.3. Some of the lower energy bands (at a binding energy of  $\sim -11 \text{ eV}$ ) can be viewed as the corresponding bonding states between Sb s and S s and p states. Overall, there is a strong match between the density of states and valence band XPS data. The qualitative similarities between the electronic structure of CuSbS<sub>2</sub> and NaSbS<sub>2</sub> become less distinctive, however, when looking at the band structure, the influence of the crystal structure becomes



Figure 3.6: Electronic band structure of NaSbS<sub>2</sub>, calculated using HSE06+SOC; valence band is in blue, conduction band in orange and E=0 is set to the valence band maximum. The notation of Bradley and Cracknell is used for identifying special k-points in the C2/c Brillouin zone.<sup>124</sup>

Figure 3.6 shows the electronic band structure of NaSbS<sub>2</sub>. It can be seen that at the Y point, the fundamental band gap is direct and has a magnitude of 1.585 eV. This is close to the ideal range for maximising the theoretical efficiency ( $\sim 1.0 \text{ eV}$  to 1.5 eV) and this value is also in good agreement with the experimentally measured optical gap of 1.73 eV. In addition, the fundamental band gap is also consistent with the previously reported band gap value of 1.58 eV by Bhattacharya *et al.*, obtained using Engler-Vosko LAPW method.<sup>125</sup> In Figure 3.6, there is a mix of highly disperse regions around the band edges with comparatively flat regions elsewhere amongst the valence and conduction bands, noticeably, the conduction band at M is almost degenerate with the conduction band minimum at Y. This structural feature is usually described as a 'multivalley', which has been reported in previous research studies for allowing a relatively high joint density of states and good charge carrier mobility, enabling a stronger absorption, all these properties are highly desirable for solar absorber materials, but they

can often be mutually exclusive.<sup>126</sup>

As-synthesized powder sample of NaSbS<sub>2</sub> was pressed into two identical pellets, A and B, for measuring the electrical conductivity via different approaches. Pellet A was measured directly using a Hall-effect four point probe machine whereas pellet B was first sintered at 400 °C for 2 h prior to the conductivity measurement. A detailed description of Hall-effect measurement can be found in Chapter 2.6. The Hall voltage was recorded in the measurement and it was induced upon a magnetic flux density of 0.58 T, however the induced voltage was measured to be negligible in both pellets A and B, causing the results to be unreliable. Repeated measurements also gave the same results, in which the induced Hall voltage was negligible. Alternatively, molten NaSbS<sub>2</sub> was obtained upon continuous heating of the powder at 800 °C and it was also measured on the Hall-effect four point probe machine, yet a similar outcome was achieved, in which the induced Hall voltage was too small to give any reliable and accurate data. As a consequence, it is highly likely that stoichiometric NaSbS<sub>2</sub> powders produced via high temperature solid-state synthesis are non-conductive. Another possibility could be that the pellets made using the original powder sample were unable to reach the required density due to the nature of a powder material, resulting in a large number of grain boundaries present inside the pellets. Despite the lack of success in measuring the electrical conductivity of NaSbS<sub>2</sub> powder, future work can be done on densifying the pellets to minimise the effects of grain boundaries, changing the stoichiometry of NaSbS<sub>2</sub> and modifying the synthesis method, for example obtaining thin films of NaSbS<sub>2</sub>.

The hole and electron effective masses can be estimated from the band structure of NaSbS<sub>2</sub> via computational methods and they often indicate the electronic properties of a material such as the electrical conductivity and charge carrier transport properties. The effective masses of both holes and electrons of NaSbS<sub>2</sub> are predicted to be relatively low, in the range of  $0.192m_0 - 0.193m_0$ , in comparison to other solar absorber materials, as indicated by the local dispersion at the band edges, and they are indeed reasonably ideal for a solar absorber candidate.<sup>127</sup> Having high carrier mobilities in a

Hall-effect measurement would typically result in low effective masses of both charge carriers, however our stoichiometric as-synthesised powder samples are not demonstrating sufficient conductivity, thus it is not possible to compare the charge carrier mobilities with the calculated effective masses of charge carriers in this case.



Figure 3.7: Diffuse reflectance spectra showing Kulbeka-Munk function (a) F(R) and (b)  $F(R)^2$  of as-synthesised NaSbS<sub>2</sub> powder.

Graphs of F(R) and  $F(R)^2$  plotted against energy are demonstrated in Figure 3.7, the absorption edge in each of these plots was extrapolated to the x-axis (y=0) in order to yield the relative absorption values respectively  $E_1$  and  $E_2$ . Extrapolated absorption values in F(R) and  $F(R)^2$  plots were found to be 1.53 eV and 1.63 eV respectively. According to the Poeppelmeier method, the optical band gap value can be obtained with the following expression:  $E_g = 2E_2 - E_1$ , hence resulting in a band gap of 1.73 eV. This is consistent and in excellent agreement with the previously reported experimental band gap of ~1.7 eV from Rahayu *et al.* based on NaSbS<sub>2</sub> nanoparticles.



Figure 3.8: Optical absorption coefficient (solid blue line) of NaSbS<sub>2</sub>. The position of the fundamental band gap is marked by the dotted line.

The theoretical optical behaviour of the system is often described by the absorption coefficient, which is plotted in Figure 3.8. Despite there being a strong absorption at 2.5 eV and beyond in the same figure, the absorption is much lower than expected in the crucial energy range necessary for a functional solar absorber material, located just above the fundamental band gap (represented by the dashed line in Figure 3.8). This originates from the forbidden optical transitions from valence band maximum to conduction band minimum and from valence band minimum to the next conduction band at Y. As such, the lowest direct transition is not available until 1.77 eV where the transition occurs from valence band to conduction band along the Y to V. Therefore the lowest direct transition represents the theoretical optical gap, and matches very well with our optical gap obtained experimentally (1.73 eV), as discussed above. These forbidden transitions result in NaSbS<sub>2</sub> having a relatively low absorption coefficient in the crucial region of the solar spectrum. As a consequence, it will cause significant impact upon the material's ability to act as a useful and efficient solar absorber, especially

within a 'thin-film' style structure.

Additionally, it is essential to assess the efficiency and functionality of NaSbS<sub>2</sub> being a solar absorber material, the Spectroscopically Limited Maximum Efficiency (SLME) designed by Yu and Zunger can determine the theoretical efficiency of a thin-flim solar cell composed of NaSbS<sub>2</sub>.<sup>128,129</sup> The SLME value of NaSbS<sub>2</sub> is estimated to be 11.50 % for a film thickness (*L*) of 200 nm, this value however compares poorly with other emerging and prominent solar absorber materials as well as most commercial solar absorber materials, of which they often exhibit SLME values above 20 %.<sup>129–131</sup>

Refractive index is also a crucial feature in determining the suitability of a solar absorber material within a solar cell. This idea was first proposed by Blank *et al.*, which states that the refractive index influences the resultant external properties, for example the current density, in the calculation of a theoretical efficiency limit.<sup>132</sup>

NaSbS<sub>2</sub> has a moderate refractive index, as predicted by high-throughput computational method. As such, the predicted solar cell efficiency would differ significantly upon how the front surface of the absorber is being modelled, either as flat or as a Lambertian scatterer: the flat surface values give a low theoretical efficiency, similar to the SLME value regardless of the optimal thickness of absorber material. On the other hand, the theoretical efficiencies from the Lambertian model are more promising with efficiency values comparable to those of other emerging and prominent solar absorber materials. Yet the low absorption coefficient of bulk NaSbS<sub>2</sub> has proved to be the biggest limitation to achieving a reasonable solar cell efficiency. As such, bulk NaSbS<sub>2</sub> is unable to reach optimal efficiencies within a thin-film style structure, further progress may be limited unless relative thick layers of material are used despite the fact that initial solar cells being produced are promising and obtained moderate solar cell efficiencies. The strong influence of the surface scattering upon the cell efficiency will encourage texturing of a film's surface or downsizing the structure to nano-scale may enhance the cell efficiencies.



Figure 3.9: Phonon dispersion curve of NaSbS<sub>2</sub>, calculated using the PBEsol functional.

Phonon dispersion curve of NaSbS<sub>2</sub> was calculated and is displayed in Figure 3.9. Analogous to NaSbS<sub>2</sub>, compounds in the ABX<sub>2</sub> (A = Ag, Na; B = Sb, Bi; X = Se, Te) family all have a rocksalt structure with 1+ and 3+ cations located over the cation site within the structure, these compounds have been previously highlighted to have desirable feature of low lattice thermal conductivities as a result of the Sb lone pair.<sup>133,134</sup> This prompts the potential application of NaSbS<sub>2</sub> as a thermoelectric material and further work is necessary to be carried out in order to examine the thermoelectric properties of NaSbS<sub>2</sub>.<sup>135,136</sup>

### 3.4 Conclusion

Phase pure NaSbS<sub>2</sub> powders were synthesised via high temperature solid state method, our experimental and theoretical lattice parameters are in good agreement with previously reported structures. The electronic band structure of NaSbS<sub>2</sub> generated by Density Functional Theory (DFT) method demonstrates a direct fundamental band gap of 1.59 eV and a theoretical optical band gap of 1.77 eV, both values are consistent

with the experimental band gap of 1.73 eV obtained from UV-Vis diffuse-reflectance measurements where the data was transformed using the Poeppelmeier method. The experimental optical band gap of NaSbS<sub>2</sub> is slightly higher than the ideal band gap for a single-junction solar absorber material. Theoretical DFT calculations have also shown that NaSbS<sub>2</sub> has a relatively low and weak absorption coefficient just above the band gap due to forbidden transitions at the Y point. In order to further assess the optical properties of NaSbS<sub>2</sub>, the Spectroscopically Limited Maximum Efficiency (SLME) of NaSbS<sub>2</sub> is estimated to be 11.5 % assuming a film thickness of 200 nm, this value is significantly lower than than the typical value for other prominent and commercial solar absorber materials, which all possess a SLME value of 20 % and above. New method to examine the relationship between film thickness and theoretical solar cell efficiency proposed by Blank et al. demonstrates that the efficiency can be greatly enhanced using a thicker film or via surface engineering of a film. This should inspire new research interest in regards to future work on NaSbS<sub>2</sub> being used as a solar absorber material. Combining all aspects and properties, optical and electronic in particular, of NaSbS<sub>2</sub>, it may not be the best candidate for single-junction solar cell applications. However, the electronic band structure of NaSbS<sub>2</sub> exhibits areas of both low and high dispersion, together with near-degenerate points within the conduction point at Y and M, often known as a multi-valley band structure. This specific feature has been previously reported in relation to a material having an optimal thermoelectric behaviour, thermoelectric measurements can identify the desired properties including the Seebeck coefficient and electrical conductivity of NaSbS<sub>2</sub>, if these properties are deemed suitable, NaSbS<sub>2</sub> may become a potential candidate in thermoelectric applications.<sup>137</sup>

# **Chapter 4**

# GaSbO<sub>4</sub>

## 4.1 Transparent-conducting Oxide



Figure 4.1: The unit cell structure of GaSbO<sub>4</sub> with Ga atoms in orange, Sb atoms in teal and O atoms in purple. The black line indicates the unit cell boundary.

First reported in 1975, structural and magnetic properties of GaSbO<sub>4</sub> were investigated by Donaldson *et al.* along with other Sb-containing compounds with the same MSbO<sub>4</sub> structure, where M = Cr, Fe, Rh and Al. These compounds were all found to have a tetragonal structure similar to that of rutile TiO<sub>2</sub> and hence they were called random rutiles. The randomness in the name, as opposed to rutile TiO<sub>2</sub>, suggested that it originated from the random occupancy of the edge-sharing atoms, Sb and Ga atoms within the crystal lattice, thus the exact occupancy of these cations is not clear.<sup>138</sup> The lack of detailed structural analysis in the previous study has prompted the motivation to examine the structural properties of GaSbO<sub>4</sub>, the cation distribution in particular. Since Sb(V) cations share the same electronic structure as Sn(IV), In(III) and Zn(II) in SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub> and ZnO respectively, theoretically speaking GaSbO<sub>4</sub> can become a unique transparent-conducting oxide (TCO) material behaving similarly or even perform better in comparison to conventional TCO materials. In this chapter, the cation ordering in GaSbO<sub>4</sub>, particularly in the c-direction with respect to the GaSbO<sub>4</sub> lattice will be investigated in great detail along with our computational collaborators using a wide range of theoretical and experimental characterisation techniques specialising in solid state chemistry. The combined analysis will shed light upon the different promising properties and suitability of GaSbO<sub>4</sub> to become the next generation TCO material.

## 4.2 Experimental Methodology

0.3913 g of Ga<sub>2</sub>O<sub>3</sub> ( $\geq$ 99.99 %, Sigma-Aldrich) and 0.6087 g of Sb<sub>2</sub>O<sub>3</sub> ( $\geq$ 99 %, Sigma-Aldrich) were ground together in an agate mortar and pestle. The stoichiometric mixture was transferred to an alumina crucible and heated in air at 1100 °C for 24 h with a heating and cooling rate of 10 °C min<sup>-1</sup>.

$$Ga_2O_3 + Sb_2O_3 + O_2 \longrightarrow 2GaSbO_4$$
### 4.3 Results and Discussion

In order to reveal the ordering in GaSbO<sub>4</sub>, various models were proposed using Monte Carlo and cluster expansion by the Scanlon Materials Theory Group, these simulated models are known as the ground state structure, semi-disordered and fully disordered "Special Quasi-random Structures" (SQS) respectively.

Prior to computing various GaSbO<sub>4</sub> structures for DFT calculations, an on-lattice model was generated using the "Alloy Theoretic Automated Toolkit" (ATAT) by Scanlon Materials Theory Group. This approach treats the GaSbO<sub>4</sub> system as a rigid lattice model where Sb and Ga can occupy any of the cation sites within the lattice and this lattice model will be optimised in the *ab initio* calculations in order to generate a ground-state structure. In addition, Monte Carlo calculations were also employed together with cluster expansion data based upon DFT calculations to generate the "Special Quasi-random Structures". As such, a semi-disordered and fully disordered SQS were generated respectively to represent the different extent of disordering in the GaSbO<sub>4</sub> structure.



Figure 4.2: (a) Powder X-ray diffraction pattern of GaSbO<sub>4</sub> and observed pattern from standard structure with the difference between the experimental and calculated intensities shown in purple, (b) simulated PXRD patterns of ground-state, semi-disordered and fully-disordered SQS structures respectively.

Rietveld refinement was performed based on the fully-disordered random rutile structure (*P42/mnm*), which is also the only literature structure available. In Figure 4.2 the refined patterns showed no evidence of secondary phase formation, indicating that the as-synthesised GaSbO<sub>4</sub> was phase pure. Lattice parameters of GaSbO<sub>4</sub> were also generated using *ab initio* calculations with the PBEsol XC-functional and shown together with the experimental and literature lattice parameter values in Table 4.1. There is an excellent agreement ( $\leq 1\%$ ) between the experimental, literature and simulated lattice parameter values. In addition, the PXRD data of GaSbO<sub>4</sub> has ruled out the possibility of the structure adopting the ground state structure due to a lack of resemblance. As a result, it is likely that GaSbO<sub>4</sub> adopts either the semi-disordered or fully disordered structure.

Table 4.1: Experimental,	literature a	and si	mulated	lattice	parameter	values of	GaSbO <sub>4</sub> .
All values are in Å							

	Experimental	Literature <sup>138</sup>	PBEsol
	(Å)	(Å)	(Å)
a	4.612(2)	4.599(9)	4.622
С	3.045(4)	3.035(10)	3.064



Figure 4.3: XPS spectra of (a) Ga 2p and (b) Sb 3d with overlapping O1s regions.

High resolution XPS spectra of GaSbO<sub>4</sub> are shown in Figure 4.3. The Ga 2*p* scan was composed of a spin-orbit doublet, a higher energy Ga  $2p_{1/2}$  component at 1144.5 eV and lower energy Ga  $2p_{3/2}$  component at 1117.6 eV, which was consistent with Ga(III) species.<sup>139</sup> Similarly, the Sb 3*d* scan was also composed of a spin-orbit doublet with a higher energy Sb  $3d_{3/2}$  component at 539.9 eV and lower energy Sb  $3d_{5/2}$  component at 530.5 eV overlapping with O 1s regions. Sb  $3d_{5/2}$  component was constrained to the Sb  $3d_{3/2}$  component according to the area ratio of 1.5 and the energy separation of 9.39 eV, the remaining area of the lower energy peak was attributed to oxygen. However, it is difficult to distinguish between Sb(III) and Sb(V) states due to the small difference between the binding energies of each Sb state. As a result, it is inconclusive as to whether Sb(III) or Sb(V) are present on the surface and it is possible that both Sb species coexist on the surface of GaSbO<sub>4</sub>.<sup>117</sup> Regardless, Sb(III) have larger ionic radii than Sb(V), the presence of Sb(III) in the bulk of material would significantly distort the lattice and such effect would be observed in the PXRD pattern of GaSbO<sub>4</sub>, hence there is no direct indication that Sb(III) are present in the bulk of GaSbO<sub>4</sub>.<sup>140</sup> Therefore, we assume Sb(V) are the only species present in the bulk of the material and mostly occupied on the surface of GaSbO<sub>4</sub>.

The surface composition of GaSbO<sub>4</sub> was quantified using the area of each individual component and their corresponding relative sensitivity factors (R.S.F), the atomic surface composition of Ga, Sb and O was found to be 18.5%, 22.4% and 59.1% respectively, suggesting that there is segregation of Sb on the surface, which is typically observed in Sb compounds.<sup>141</sup> The slightly non-stoichiometric ratio of oxygen on the surface could be caused by the presence of Sb(III) on the surface, in which Sb(III) is being oxidised, however, the amount of Sb(III) are assumed to be significantly less than than Sb(V) on the surface. Possible reasons to this observation include the presence of SbO<sub>x</sub> phases in the sample and they are not detected by PXRD; genuine segregation of Sb(V) on the surface of GaSbO<sub>4</sub>.



Figure 4.4: Experimental and simulated valence band XPS spectra of as-synthesised GaSbO<sub>4</sub> and proposed ground state, semi-disordered and fully-disordered structures respectively.



Figure 4.5: A graph showing the experimental valence band XPS spectrum of assynthesised GaSbO<sub>4</sub> alongside with calculated density of states of the proposed ground state structure plotted in the binding energy range of 0 eV to 15 eV.

As the electronic structure of GaSbO<sub>4</sub> is correlated and dependent upon the physical unit cell structure, i.e. the cation ordering, in GaSbO<sub>4</sub>, XPS valence band measurements would allow us to probe into the electronic structure, namely the density of states, and by comparing the differences in electronic structures of various simulated models, we can further deduce the overall structure of GaSbO<sub>4</sub>. As such, simulated valence band spectra of the proposed ground state, correlated-disordered and fully disordered structures of GaSbO<sub>4</sub> were aligned at 0 eV and displayed in Figure 4.4. Experimental valence band data collected from XPS experiment were aligned approx-

imately to the simulated data obtained by Scanlon Materials Theory Group, there is a noticeable characteristic shoulder region between 4 eV to 6 eV in the experimental data. The density of states of the proposed ground state GaSbO<sub>4</sub> structure is shown in Figure 4.5. As a result, we focus on identifying any characteristic features in the valence band data and of which, only the proposed ground state valence band data has a small shoulder region between 4 eV to 6 eV. Due to lack of distinctive shoulder features in other valence band spectra, the slight resemblance of the distinctive shoulder region between the experimental data and the proposed ground state structure evidently indicates that GaSbO<sub>4</sub> adopts a ground state structure.



Figure 4.6: Plots of GaSbO<sub>4</sub> showing diffuse-reflectance data transformed via Kulbeka-Munk function, (a) F(R) and (b)  $F(R)^2$  against energy.



Figure 4.7: Simulated optical absorption spectra with green, orange and blue line corresponding to ground state, semi-disordered and fully-disordered structures, each labelled as GS, ISQS and SQS respectively. Dotted lines show the fundamental band gap values of each proposed structure.

Figure 4.6 shows the extrapolated values for F(R) and  $F(R)^2$  to be 3.55 eV and 3.68 eV respectively. According to the Poeppelmeier method, the optical band gap value  $E_{g}$ =  $2E_2 - E_1$  and hence the band gap of as-synthesised GaSbO<sub>4</sub> was found to be 3.81 eV. In order to understand how the ordering of GaSbO<sub>4</sub> effect upon the optical properties, fundamental band gap values were calculated to be 3.46 eV, 3.03 eV and 2.03 eV for the ground state, semi-disordered and fully-disordered structures respectively in Figure 4.7. The fundamental band gap of a material is defined as the gap strictly between valence band maximum and conduction band minimum regardless of the probability of the electronic transition between the two, and it can be graphically determined as the point before any absorption of light occurs in a simulated absorption spectrum. Optical band gap is usually bigger than a fundamental band gap because optical band gap is usually the lowest accessible energy transition. Therefore, having compared all the optical data and taken into consideration the fact that optical band gaps are

always bigger than fundamental band gaps of a material, it is plausible that GaSbO<sub>4</sub> has either the ground state or semi-disordered structure due to a closer resemblance between the calculated and experimental band gap values. In addition, Scanlon Materials Theory Group calculated GaSbO<sub>4</sub> to have a low conduction-band effective mass between 0.22 to 0.35 m<sub>e</sub> and a large electron affinity of 5.5 eV, suggesting it would be tolerant to the degree of disorder as a n-type material.

### 4.4 Conclusion

Other computational techniques have identified a range of physical properties that would benefit GaSbO<sub>4</sub> as a potential TCO candidate, these properties include a low conduction-band effective mass and large electron affinity. Further to that, these properties are not likely to be affected by the degree of disorder within the structure of GaSbO<sub>4</sub>, hence making it a very robust TCO candidate. Having said that, GaSbO<sub>4</sub> is likely to have some degree of disordering within the structure and nonetheless, GaSbO<sub>4</sub> has numerous desirable properties such as a large band gap for a new n-type TCO material.

## **Chapter 5**

# BaBi<sub>2</sub>O<sub>6</sub>

### 5.1 Thermoelectric oxides

As a thermoelectric device requires both n-type and p-type materials, it is challenging to design n-type thermoelectric materials as they typically have zT values far below one- the minimum limit for practical applications. Perovskite-type oxides such as SrTiO<sub>3</sub> and CaMnO<sub>3</sub> are the most promising n-type thermoelectric oxide materials, SrTiO<sub>3</sub> in particular can be tailored by layering which give rise to SrO(SrTiO<sub>3</sub>)<sub>n</sub> or doping with niobium and lanthanum. SrTiO<sub>3</sub> was long found to exhibit a large thermopower and high electrical conductivity due to carrier effective mass in two orders of magnitude larger than that of other n-type thermoelectric materials, possibly caused by the predominant Ti 3d states in the conduction band and O 2p orbitals in the valence band.<sup>142,143</sup> Despite the fact that they display excellent electronic transport properties and are stable at high temperatures, high thermal conductivity in SrTiO<sub>3</sub> is yet to be overcome. Even though zT values has only been achieved up to 0.37 at 1000 K for Nb doped SrTiO<sub>3</sub>, this value is comparable to that of the other candidate- doped ZnO.<sup>69,144–146</sup> In designing new efficient n-type thermoelectric materials, the usual criteria apply: they have to be earth abundant, non-toxic and economically friendly in large scale production. Most importantly, these potential materials should have reasonable *zT* values for practical thermoelectric applications, this can be achieved by nano-engineering the structure of a material, thus maintaining a balance between high electrical conductivity and large thermopower as well as low lattice thermal conductivity.<sup>147,148</sup>



Figure 5.1: The unit cell structure of  $BaBi_2O_6$  along (a) (100) and (b) (001).

Having a PbSb<sub>2</sub>O<sub>6</sub>-type structure with edge-sharing BiO<sub>6</sub> octahedra and interlayed  $Ba^{2+}$  octahedrally coordinated in the adjoining layers, high photocatalytic activity and an experimental band gap of 2.6 eV,  $BaBi_2O_6$  was first considered to be a potential transparent conducting oxide candidate.<sup>149,150</sup> Due to the electronic structure of Bi(V), the system is expected to have disperse CBM and hence, high conductivity. The lattice thermal conductivity is also expected to be lower in this layered system while most TCO materials being studied, are limited by their high lattice thermal conductivities.

This begs the question: could  $BaBi_2O_6$  be used in thermoelectric application instead? Recent computational studies performed by Scanlon Materials Theory group have calculated a direct band gap of 2.8 eV, which is shown in Figure 5.2, and low effective masses in and across the layers. Having fulfilled the basic requirements for a potential thermoelectric material,  $BaBi_2O_6$  is also predicted to have low lattice thermal conductivities ( $<1 W m^{-1} K^{-1}$ ) at temperatures above 800 K as shown in Figure 5.3. This would overcome the high lattice thermal conductivity of other thermoelectric oxides such as SrTiO<sub>3</sub> and CaMnO<sub>3</sub>. Despite the fact that it is a layered structure, Figure 5.4 demonstrates the relatively isotropic *zT* values, calculated by Scanlon Materials Theory Group, at an ideal carrier concentration of  $10^{20} cm^{-3}$  across all directions, making it an extremely attractive n-type thermoelectric material with great potentials in high temperature applications. Due to the high earth abundancy and non-toxicity of barium and bismuth, the other aim of this project is to synthesize materials such as BaBi<sub>2</sub>O<sub>6</sub> based on new computational findings and therefore, evaluate the potential applications.



Figure 5.2: Band Structure of BaBi<sub>2</sub>O<sub>6</sub>.



Figure 5.3: Lattice thermal conductivity diagrams of  $BaBi_2O_6$  at various temperatures.



Figure 5.4: The variation of zT values of BaBi<sub>2</sub>O<sub>6</sub> along different carrier concentrations in the temperature range between 300 K to 1300 K.

### 5.2 Experimental Methodology

NaBiO<sub>3</sub> was synthesized prior to the production of BaBi<sub>2</sub>O<sub>6</sub> due to the presence of impurities in commercially available NaBiO<sub>3</sub>. Firstly, 10.0253 g of Bi(NO<sub>3</sub>)<sub>3</sub> · 9 H<sub>2</sub>O (≥99 %, Sigma-Aldrich) was dissolved and stirred in  $20 \text{ cm}^3$  1M HNO<sub>3</sub>.  $1 \text{ cm}^3$  of Bi(NO<sub>3</sub>)<sub>3</sub> solution was added to  $20 \text{ cm}^3$  15M NaOH solution and white precipitate of Bi(OH)<sub>3</sub> formed immediately in the mixture.

$$\operatorname{Bi}(\operatorname{NO}_3)_3 + 3\operatorname{NaOH} = \operatorname{Bi}(\operatorname{OH})_3 + 3\operatorname{NaNO}_3$$

Bi(OH)<sub>3</sub> precipitate was filtered off quickly using a G3 sintered glass funnel and the filtration was repeated with a clean funnel until all Bi(OH)<sub>3</sub> was filtered. Bi(OH)<sub>3</sub> was washed with distilled water to obtain neutral precipitate, which was then desiccated under vacuum overnight. 2.2392 g of dried Bi(OH)<sub>3</sub> was added to  $27.7 \text{ cm}^3 10 \%$  NaClO solution and stirred for 30 min.  $29.6 \text{ cm}^3 11M$  NaOH was also added to the reaction mixture and was left to stir for a minimum of 3 days.

$$Bi(OH)_3 + NaClO + NaOH = NaBiO_3 + 2H_2O + NaCl$$

The mixture was filtered off after stirring using a G4 glass sintered funnel and washed with distilled water until the filter was neutral. The NaBiO<sub>3</sub> obtained was also washed with 100 cm<sup>3</sup> diethyl ether and dried on the funnel overnight to remove any remaining solvents. To synthesize BaBi<sub>2</sub>O<sub>6</sub>, 1.5009 g of BaCl<sub>2</sub> · 2 H<sub>2</sub>O ( $\geq$ 99 %, AnalaR) and 0.4307 g of NaBiO<sub>3</sub> were placed in a 40 mL Teflon-lined autoclave with atomic ratio of Ba:Bi being 4:1. 18 cm<sup>3</sup> H<sub>2</sub>O was added to the mixture and the autoclave was heated at 90 °C at a rate of 2.5 °C min<sup>-1</sup> for 48 h, and cooled at a rate of 10 °C min<sup>-1</sup>. The products were filtered, washed with water and acetone and left to dry on the filter.

### 5.3 Results and Discussion

The initial synthesis of BaBi<sub>2</sub>O<sub>6</sub> was found to be challenging as one of the precursor materials NaBiO<sub>3</sub> was no longer commercially available and this material has not been very well-researched in the science community. Just over a decade ago, a paper published by Pan *et al.* has successfully synthesized NaBiO<sub>3</sub> with a maximum purity of 92.8 % and precisely recorded the experimental procedures in details.<sup>151</sup> However, initial attempts to reproduce the results were unsuccessful, it was discovered that some quantities of reagents and experimental conditions that Pan *et al.* used were inaccurate, or rather unrealistic, for example, incorrect units and conversion between units were presented in the literature. On the other hand, synthesis of BaBi<sub>2</sub>O<sub>6</sub> was first published by Mizoguchi *et al.*, unfortunately there was no mention of the exact quantities used in synthesis. Nevertheless, NaBiO<sub>3</sub> was successfully synthesized once the precise atomic ratio of Ba:Bi needed to synthesizeBaBi<sub>2</sub>O<sub>6</sub> was found on ICDD. All experimental procedures can be found in Methodology section.



Figure 5.5: PXRD pattern of as-synthesized and simulated structure of BaBi<sub>2</sub>O<sub>6</sub> shown in brown and black respectively.

Figure 5.5 shows the powder XRD pattern of as-synthesized  $BaBi_2O_6$  refined against the DFT calculated model with a space group P-*31m*, as the structure is consistent with the PbSb<sub>2</sub>O<sub>6</sub> structure type. There was no unassigned peaks observed, which indicated that as-synthesised  $BaBi_2O_6$  is phase pure. The relative broadness of peaks indicated that the material has a low crystallinity. The overall PXRD and peak intensity of as-synthesized  $BaBi_2O_6$  suggested that ratio of Ba:Bi is 1:2. In contrast, the first PXRD pattern published by Mizoguchi *et al.* showed different relative intensity to the as-synthesized BaBi<sub>2</sub>O<sub>6</sub> as well as DFT calculated model, possibly due to lattice defects or differences in precursor materials.<sup>149</sup>

	Experimental BaBi <sub>2</sub> O <sub>6</sub>	Mizoguchi BaBi <sub>2</sub> O <sub>6</sub> <sup>149</sup>		
	(Å)	(Å)		
a	5.577(4)	5.576(3)		
c	5.796(7)	5.785(7)		

Table 5.1: Lattice parameters of as-synthesized  $BaBi_2O_6$  and previously recorded  $BaBi_2O_6$  powder.\_\_\_\_\_

Table 5.2: Calculated lattice parameters of BaBi<sub>2</sub>O<sub>6</sub>, with percentage differences from experimental results.

	DFT caculated BaBi <sub>2</sub> O <sub>6</sub>	% difference from		
	(Å)	As-synthesised $BaBi_2O_6$	Mizoguchi <i>et al.</i> <sup>149</sup>	
a	5.590	-0.23	-0.25	
c	5.806	-0.17	-0.36	

Lattice parameters of as-synthesised  $BaBi_2O_6$  were obtained via Rietveld refinement and presented together with the literature values from Mizoguchi *et al.* in Table 5.1. DFT calculated lattice parameters of  $BaBi_2O_6$  are displayed in Table 5.2, where the % difference between the DFT values and as-synthesised  $BaBi_2O_6$  and Mizoguchi *et al.* respectively are also shown. Both experimental  $BaBi_2O_6$  have bigger lattice parameters in the a and c direction than the DFT calculated model, however, they were all in good agreement with less than 1% difference.



Figure 5.6: XPS spectra of (a) Ba 3d and (b) Bi 4f.



Figure 5.7: XPS spectra of (a) O 1*s* and (b) the valence band region up to -10 eV overlaying with the simulated valence band taken from calculated Density of States (DOS) plot of BaBi<sub>2</sub>O<sub>6</sub>.

XPS spectra of  $BaBi_2O_6$  are shown in Figure 5.6 and Figure 5.7 together with the curve fitting as described in the previous section. The high resolution Ba 3*d* scan showed a spin-orbit doublet with an energy difference of 15.1 eV between the higher energy  $3d_{3/2}$ 

and lower energy  $3d_{5/2}$  components, which can be typically observed in barium oxide compounds.<sup>152</sup> Similarly, the spin-orbit doublet in the high resolution Bi 4*f* scan was composed of the lower energy component  $4f_{7/2}$  at 158.7 eV and the higher energy component  $4f_{5/2}$  at 164.0 eV, indicating the presence of Bi<sup>3+</sup> in the compound. In addition, these peaks were also consistent with those observed in bismuth oxide compounds. Apart from the O 1*s* spectral component at 529.6 eV, there was also an additional O 1*s* component within the region, which could be caused by the presence of hydroxide species. The simulated and experimental valence band data shown in Figure 5.7(b) were in excellent agreement with the spectral peak at -4.9 eV corresponding to Bi 6*s* and *p* states. By adjusting the adventitious C 1*s* to 284.8 eV, Fermi level was located at 0 eV on the valence band spectrum and the valence band edge was approximated to be 2.33 eV away from the Fermi level, indicating that the Fermi level was closer to the conduction band as predicted.



Figure 5.8: Diffuse reflectance spectra showing Kulbeka-Munk function (a) F(R) and (b)  $F(R)^2$ .

Diffuse reflectance data were transformed using Kulbeka-Munk function and Figure 5.8 shows the plots of F(R) and  $F(R)^2$  against energy using the Poeppelmeier method, only the lower energy absorption edge in the same region was being considered as it

was the lowest energy absorption between valence band and conduction band edges. The absorption edge of each plot was extrapolated to the x-axis (y = 0). Extrapolated values for F(R) and  $F(R)^2$  are 2.03 eV and 2.32 eV respectively. According to the Poeppelmeier method, the band gap value  $E_g = 2E_2 - E_1$  and the band gap of BaBi<sub>2</sub>O<sub>6</sub> was found to be 2.60 eV, which is in good agreement with both the calculated band gap of 2.87 eV and previous report of 2.6 eV.<sup>149</sup>



Figure 5.9: Thermo gravimetric analysis of  $BaBi_2O_6$  from 20 °C to 1000 °C with machine artefact at low temperature.

Shown in Figure 5.9, thermo gravimetric analysis (TGA) of  $BaBi_2O_6$  displayed a loss in mass starting at around 100 °C which could be attributed to the loss of hydration of water in the sample and it was consistent with Mizoguchi *et al.*<sup>149</sup> The second loss in mass, which accounted for 4 % of the total mass, was seen at 340 °C possibly due to the loss of oxygen, however, the decomposition product remained unknown. Further decomposition of the sample occurred at around 650 °C where 5 % of the total mass was lost, indicating  $BaBi_2O_6$  decomposed and underwent further phase transitions.



Figure 5.10: PXRD patterns showing the phase transitions of  $BaBi_2O_6$  from 300  $^\circ C$  to 600  $^\circ C.$ 

Following the TGA analysis, further structural information of  $BaBi_2O_6$  was obtained by heating it from room temperature (20 °C) to various elevated temperatures as shown in Figure 5.10.  $BaBi_2O_6$  started to form a new phase at 350 °C and the phase transition continued up until 600 °C, at which point a highly crystalline phase was formed. This highly crystalline phase is likely to have  $BaBiO_{6-x}$ , specifically  $BaBiO_3$ -related structures but the exact stoichiometry is unclear. Note that the small increase in mass between 20 °C and 100 °C was due to an instrument effect, in which a drift was created on the balance upon heating.

### 5.4 Conclusion

With all the promising features, it is clear that  $BaBi_2O_6$  is a very attractive n-type thermoelectric material. The highly disperse conduction band feature, relatively good *zT* value across a wide range of temperature, ease of fabrication as well as the high earth abundancy and low toxicitiy of its constituent elements, these desirable properties have made  $BaBi_2O_6$  a very strong contender in the race to discover the next best thermoelectric material. However, due to decomposition at above 300 °C,  $BaBi_2O_6$  is thermally and chemically stable at low temperatures, resulting in a *z*T value of around 0.2 (at 330 °C).  $BaBi_2O_6$  still has a relatively low thermal conductivity and reasonable electrical conductivity at 330 °C, making it equally competitive as the other conventional thermoelectric materials such as  $SrTiO_3$ . In fact, there is great potential for  $BaBi_2O_6$  to become a novel low temperature n-type thermoelectric material and other research interests have shown that by doping it with La would theoretically lower the thermal conductivity even further and result in a higher *zT* value.

# **Chapter 6**

# ZnSb<sub>2</sub>O<sub>6</sub>

## 6.1 Transparent-conducting Oxide



Figure 6.1: The unit cell structure of  $ZnSb_2O_6$  with Zn atoms in blue, Sb atoms in pink and O atoms in green.

One of the more detailed reports of  $ZnSb_2O_6$  was published in the same paper with  $GaSbO_4$  by Donaldson *et al.* and unlike  $GaSbO_4$ , it was found to have an ordered

tri-rutile structure in which the edge-sharing atoms are in order of Zn-Sb-Sb-Zn while the body-centered atoms alternate in order of Sb-Zn.<sup>138</sup> Other compounds such as MgSb<sub>2</sub>O<sub>6</sub>, CoSb<sub>2</sub>O<sub>6</sub>, NiSb<sub>2</sub>O<sub>6</sub> and CuSb<sub>2</sub>O<sub>6</sub> were also investigated due to all of them having the same tri-rutile structures. It is important to mention that the presence of Sb(V) in ZnSb<sub>2</sub>O<sub>6</sub> results in highly dispersive CBM and a higher conductivity.<sup>100</sup>

First discovered by a research team in Japan, Nishiyama et al. examined the thermoelectric properties of ZnSb<sub>2</sub>O<sub>6</sub> and various n-doped ZnSb<sub>2</sub>O<sub>6</sub>, they discovered that ZnSb<sub>2</sub>O<sub>6</sub> had very low electrical conductivity whereas n-type (Co, Ni, Cu) doped ZnSb<sub>2</sub>O<sub>6</sub> samples demonstrated much higher electrical conductivity and higher Seebeck coefficient in the range between  $250 \,\mu\text{V}\,\text{K}^{-1}$  to  $350 \,\mu\text{V}\,\text{K}^{-1}$ .<sup>153</sup> It only took six years until Mizoguchi et al. published further details on the structural, electronic and optical properties. They observed an optical absorption in the near-IR region and a wide band gap of 3.5 eV, 0suggesting the potential of ZnSb<sub>2</sub>O<sub>6</sub> in becoming a new TCO material.<sup>149</sup> Based on the experimental results, it was concluded that in undoped ZnSb<sub>2</sub>O<sub>6</sub>, the carrier concentration, oxygen vacancies in this case, decreased as the temperature increased while in the n-type doped ZnSb<sub>2</sub>O<sub>6</sub> samples, the divalent dopant ions were thought to have the carrier electrons and thus, maintain the charge balance within the lattice. Further investigation into the carrier generation in ZnSb<sub>2</sub>O<sub>6</sub> proposed that the crystallinity would affect the carrier generation and the conductivity was strongly dependent on the cation ordering in the lattice, hence substitutional doping of Zn ions in the lattice would generate electron carriers.<sup>154</sup> This result is coherent with the previous conclusion that substitutional doping of Zn sites in the lattice would increase the electrical conductivity, however, the choice of dopant must be taken into consideration when designing a new thermoelectric material as the effective mass of the dominant charge carrier would affect the overall charge carrier mobility in the same system.

In this chapter,  $ZnSb_2O_6$  and new n-type doped  $ZnSb_2O_6$  materials will be investigated fully with respect to the structural, electronic, optical and thermoelectric properties, the mechanism of dopant in the  $ZnSb_2O_6$  system will also be explained together in a combined computational and experimental analysis.

### 6.2 Experimental Methodology

Stoichiometric amounts of reactants, 0.2184 g of ZnO ( $\geq 99 \%$ , Sigma-Aldrich) and 0.7820 g of Sb<sub>2</sub>O<sub>3</sub> ( $\geq 99 \%$ , Sigma-Aldrich) were ground together in an agate mortar and pestle. The stoichiometric mixture was heated in alumina crucibles at 1100 °C for 48 h in air.

#### MSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> where M= AI, Ga, In, Fe and Cr

Stoichiometric ratios of  $MSbO_4$ : $ZnSb_2O_6$  mixtures were prepared by grinding their binary oxides ( $Al_2O_3$ ,  $Ga_2O_3$ ,  $Sc_2O_3$ ,  $Cr_2O_3$ ) and  $In(NO_3)_3$  ( $\geq 99.99\%$ , Sigma-Aldrich) with  $Sb_2O_3$  and ZnO. All the mixtures were transferred to different alumina crucibles and heated in air between 700 °C and 1100 °C for 36 h to 60 h.

$$\frac{x}{2}M_2O_3 + (1-x)ZnO + (1-\frac{x}{2})Sb_2O_3 + (1-\frac{x}{2})O_2 \longrightarrow (MSbO_4)_x(ZnSb_2O_6)_{1-x}$$

$$x \operatorname{In}(\operatorname{NO}_3)_3 + (1-x) \operatorname{ZnO} + (1-\frac{x}{2}) \operatorname{Sb}_2 \operatorname{O}_3 + (3-x) \operatorname{O}_2 \longrightarrow (\operatorname{InSbO}_4)_x (\operatorname{ZnSb}_2 \operatorname{O}_6)_{1-x} + 3\operatorname{NO}_2 \xrightarrow{} (\operatorname{InSbO}_4)_x (\operatorname{ZnSb}_2 \operatorname{O}_6)_{1-x} + 3\operatorname{NO}_2 \xrightarrow{} (\operatorname{InSbO}_4)_x (\operatorname{ZnSb}_2 \operatorname{O}_6)_{1-x} \xrightarrow{} (\operatorname{InSbO}_4)_x (\operatorname{I$$

where x corresponds to the % used throughout this chapter.

### NiSb<sub>2</sub>O<sub>6</sub>:ZnSb<sub>2</sub>O<sub>6</sub>

 $NiSb_2O_6$ : $ZnSb_2O_6$  mixtures were prepared by grinding NiO ( $\geq$  99.99 %, Sigma-Aldrich),  $Sb_2O_3$  and ZnO together. All the mixtures were transferred to different alumina crucibles and heated in air at 1100 °C for 120 h.

### $Nb_2O_5:ZnSb_2O_6$

1% - 80% Nb doped ZnSb<sub>2</sub>O<sub>6</sub> samples were also prepared by mixing Nb<sub>2</sub>O<sub>5</sub> ( $\geq 99\%$ , Sigma-Aldrich) with ZnO and Sb<sub>2</sub>O<sub>3</sub> in the atomic ratio of 1:1 Nb:Zn. All the mixtures were transferred to different alumina crucibles and heated in air at 1100 °C for 48 h.

All samples were heated and cooled at a cooling rate of  $20 \,^{\circ}C \,^{min^{-1}}$ , and ground before further analysis.

## 6.3 Results and Discussion

### PXRD

All as-synthesised  $MSbO_4$ : $ZnSb_2O_6$  where M= Ga, Cr, Al, Fe, and In,  $NiSb_2O_6$ : $ZnSb_2O_6$ and  $Nb_2O_5$ : $ZnSb_2O_6$  powders were characterised via powder X-ray diffraction technique, phases of interest are subsequently identified in their PXRD plots and discussed in this chapter.



Figure 6.2: PXRD pattern of GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> mixtures at different Ga content, from x=0% to 20% and 80% to 100% in 5% increment.



Figure 6.3: PXRD pattern of CrSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> mixtures at different Cr content, from x=0% to 20 %, in 5 % increment, 30 % and 100 %.



Figure 6.4: PXRD pattern of AlSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> mixtures at different Al content, from x=0% to 20% and 100% in 5% increment.



Figure 6.5: PXRD pattern of FeSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> mixtures at different Fe content, from x=0% to 20% and 100% in 5% increment. Additional peaks are denoted with an asterisk.



Figure 6.6: PXRD pattern of  $InSbO_4$ : $ZnSb_2O_6$  mixtures at different In content, from x = 0% to 10% in 2% increment, 20%, and 100%. Additional peaks are denoted with an asterisk.



Figure 6.7: PXRD pattern of Ni<sub>2</sub>O<sub>6</sub>:ZnSb<sub>2</sub>O<sub>6</sub> mixtures at different Ni content, from x = 0% to 40% in 10% increment, and 100%. Additional peaks are denoted with an asterisk.



Figure 6.8: PXRD pattern of Nb<sub>2</sub>O<sub>5</sub>:ZnSb<sub>2</sub>O<sub>6</sub> mixtures at different Nb content, from x= 0 % to 20 % in 5 % increment, and 80 %. Additional peaks are denoted with an asterisk.

Shown in Figure 6.2, low % solid solutions in GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> series have adopted the ordered tri-rutile ZnSb<sub>2</sub>O<sub>6</sub> structure, whereas the high % solid solutions have the disordered random rutile GaSbO<sub>4</sub> structure, both structures have the same space group of *P42/m n m*. Similarly, low % CrSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions in Figure 6.3 have adopted ordered tri-rutile ZnSb<sub>2</sub>O<sub>6</sub> structure while high % CrSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions have the random rutile structure CrSbO<sub>4</sub>, analogous to the GaSbO<sub>4</sub> structure.

Other series such as AlSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub>, shown in Figure 6.4, despite all the low %solid solutions have the tri-rutile structure, refined lattice parameters did not change significantly upon post-XRD analysis. This suggests that AI did not incorporate into the structure due to a much smaller ionic radii (0.54 Å) than Zn(II) (0.74 Å). In the same series, 100 % AISbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solution consisted of a mixture of unknown phases. In Figure 6.5, the tri-rutile structure was predominantly present in low %FeSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions up until 15 % FeSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub>, where additional peaks appeared. These additional peaks do not correspond to any known structures. Although the tri-rutile structure has transitioned into the random rutile structure, refined lattice parameters did not change upon further addition of Fe, suggesting Fe was unsuccessfully incorporated into the ZnSb<sub>2</sub>O<sub>6</sub> structure. Similar to AlSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub>, 100 % FeSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> did not correspond to the expected FeSbO<sub>4</sub> random rutile structure, instead it contained a minor impurity phase. Shown in Figure 6.6, additional impurity peaks started to appear in 8 % InSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub>, both the lack of shifting in the peaks and difference in ionic radii of In (0.80 Å) and Zn (0.74 Å) would not result in a significant change in lattice parameters, indicating In also did not incorporate into the lattice. Despite 100 % InSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solution having a very similar structure to random rutile, additional impurity peaks, including the one at 17.6 °C, suggest the likelihood of a slightly distorted random rutile structure resulting from the different phase observed to that of GaSbO<sub>4</sub>. Phase transformation from tri-rutile to random rutile structure was incomplete in NiSb<sub>2</sub>O<sub>6</sub>:ZnSb<sub>2</sub>O<sub>6</sub> and Nb<sub>2</sub>O<sub>5</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions, demonstrated in Figure 6.7 and Figure 6.8 respectively. Impurity phases appeared at 40% and 20% Nb<sub>2</sub>O<sub>5</sub>:ZnSb<sub>2</sub>O<sub>6</sub> and NiSb<sub>2</sub>O<sub>6</sub>:ZnSb<sub>2</sub>O<sub>6</sub> respectively. The doping mechanism will be explored and discussed further in the next section.

Note that the origin of all these additional impurity peaks could not be identified through any crystallographic databases and thus, remaining unknown.
Table 6.1: A summary of doping effects in  $XSbO_4$ : $ZnSb_2O_6$  (where M= Ga, Cr, Al,Fe and In),  $NiSb_2O_6$ : $ZnSb_2O_6$  and  $Nb_2O_5$ : $ZnSb_2O_6$  solid solutions. Yes and No are denoted by Y and N respectively.

Dopant	Shift in	Valence State	Ionic Radius <sup>120</sup>	Successful Doping
_	Lattice Parameters		(Å)	
Ga	Υ	3	0.62	Y
Cr	Ν	3	0.62	Y
Al	Ν	3	0.54	Ν
Fe	Ν	3	0.65	Ν
In	Ν	3	0.80	Ν
Ni	Ν	2	0.69	Ν
Nb	Ν	5	0.64	Ν

It is interesting to note that despite both Ga(III) and Cr(III) ions having the same ionic radii and charge, only Ga series has seen a shift in lattice parameters. Summarized in Table 6.1, dopant ions with ionic radii significantly greater than 0.62 Å and a non tri-valence state did not successfully incorporate into  $ZnSb_2O_6$  lattice. These preliminary observations suggest that both valency and ionic radii of dopant ions are equally important in terms of doping mechanism. Furthermore, both Ga and Cr behave differently in their respective solid solution series, which will be discussed in the next section.

### **Composition Analysis**



Figure 6.9: Graphs showing the change in EDS measured bulk composition of (a) Ga (b) Sb and Zn in  $GaSbO_4$ :ZnSb<sub>2</sub>O<sub>6</sub> solid solutions at different nominal Ga content. Expected stoichiometric amount of each element are represented by the dotted lines.

As mentioned previously, low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> compounds have adopted the ordered tri-rutile structure in which Zn and Sb atoms occupy specific sites within the lattice. In Figure 6.9, the bulk composition was measured by Energy-Dispersive X-ray Spectroscopy (EDS) and shown in atomic ratio. Ga(III) are expected to take up mostly Zn sites in the ZnSb<sub>2</sub>O<sub>6</sub> lattice, however, the decline in Zn composition is much slower than expected, possibly due to the small presence of a poorly crystalline phase composed of Ga, Sb and Zn. In addition, reactions between the elemental constituents with air could also explain the formation of this poorly crystalline phase, which was detected by EDS and not in PXRD. The significant decrease in Sb is sought to be caused by Ga substituting Sb sites in the lattice as well as the high volatility of Sb oxides. As high % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions all have random-rutile structures, Ga(III) can substitute either Zn or Sb site in the lattice as both of these sites are thought to be crystalgraphic equivalent in the random rutile structure, resulting in Ga composition increasing, and Sb and Zn decreasing in a similar rate to the expected change in composition.



Figure 6.10: Grapsh showing the change in XRF measured bulk composition of (a) Ga (b) Sb and Zn in  $GaSbO_4$ :ZnSb<sub>2</sub>O<sub>6</sub> solid solutions at different nominal Ga content. Expected stoichiometric amount of each element are represented by the dotted lines.

X-ray fluorescence (XRF) technique was also used to measure the elemental composition of the GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions in order to draw comparison with the EDS results. In Figure 6.23, Ga, Zn and Sb composition change accordingly to the expected stoichiometric amount, only with slight deviations in Ga and Sb at high % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions respectively. Besides, Ga can take up either cystalgraphic equivalent site in the random rutile structure, specifically in the high % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions. For this reason, deviations of Ga and Sb in both Zn-rich and Ga-rich regions cab be explained by the high volatility of Ga and Sb and the likelihood of a poorly crystalline phase present in these solid solutions, similarly, it was only detected in EDS and XRF.

Overall, XRF results are in good agreement with the proposed explanation that Ga(III) are taking up Zn sites in low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions while it can substitute either Zn and Sb site in high % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions.



Figure 6.11: A graph showing the change in EDS measured bulk composition of (a) Cr (b) Sb and Zn in  $CrSbO_4$ :ZnSb<sub>2</sub>O<sub>6</sub> solid solutions at different nominal Cr content. Expected stoichiometric amount of each element are represented by the dotted lines.



Figure 6.12: A graph showing changes in EDS measured bulk composition of Sb and Zn in  $GaSbO_4$ :ZnSb<sub>2</sub>O<sub>6</sub> and CrSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions at different EDS measured bulk composition of Ga and Cr respectively.

In Figure 6.11,  $CrSbO_4:ZnSb_2O_6$  display a similar trend to the Ga series with the exception that Zn composition also decreases simultaneously with Sb in low %  $CrSbO_4:ZnSb_2O_6$  solid solutions. While the bulk Cr composition increases linearly with the nominal amount of dopant, it is significantly less than the nominal composition of Cr. For instance, there is only 10% of Cr in the bulk in a nominally 30%  $CrSbO_4:ZnSb_2O_6$  solid solution. When both Cr and Ga series are displayed together in Figure 6.12, the difference between the two series becomes more distinct. In region with low % dopant, bulk Zn composition decreases slowly in Ga series while both Sb and Zn composition decrease simultaneously in Cr series, indicating that the substitution mechanism is affected to a certain extent by the choice of dopant. Additionally, the presence of a

poorly crystalline phase in Ga series could also be affected by the choice of dopant ion. However, in region with high % dopant, both Zn and Sb bulk composition decrease significantly, this observation is consistent with the proposed explanation that random substitution of dopant is the predominant doping mechanism in these disordered, high % dopant solid solutions.



#### **Rietveld Refinement**

Figure 6.13: Graphs showing the refined unit cell volumes of GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions at different nominal (a) Ga content and (b) EDS measured composition, both compared against Vegard's Law.

PXRD patterns of  $ASbO_4:ZnSb_2O_6$  solid solutions, where A= Ga and Cr, were refined against the published structural model in the *P42/m n m* space group in Rietveld refinement using EXPGUI and GSAS software.<sup>155</sup> Peak shape, background and unit cell parameters were constantly refined throughout the process while all other parameters including composition remained unchanged. Unit cell parameters were obtained from refined structures, Ga series were shown in Figure 6.13. Phase pure compounds in other XSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> series where X= Cr, Al, In and Fe show no significant changes in the refined lattice parameters with respect to literature, which are also consistent with the PXRD patterns. Vegard's Law states that in an ideal solid solution, the lattice parameters should change linearly with the composition. Figure 6.13(a) and (b) show that in low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions, the majority of refined lattice volumes deviate positively from Vegard's Law line at different nominal and EDS measured composition of Ga respectively.

Apart from charge carriers being produced, it is possible that there are compensating defects such as oxygen vacancies ( $V_O^{..}$ ) present in the lattice. In fact, the overall doping method can be explained using Kröger-Vink notation.

$$(2+x)Ga'_{Zn} + Ga''_{Sb} + xe'$$

where x is the deviation from perfect stoichiometric coefficient.

On the other hand, high % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solutions have disordered rutiles structures where Ga can randomly substitute either Zn or Sb sites in the lattice, and their lattice volumes mostly fall on the Vegard's Law line. For this reason, it has been assumed that Ga and Sb occupy the lattice in the ratio of 50:50 in as-synthesised GaSbO<sub>4</sub>.



Figure 6.14: A graph showing the refined unit cell volumes of  $CrSbO_4$ : $ZnSb_2O_6$  mixtures at different nominal %  $CrSbO_4$  in  $ZnSb_2O_6$ .

In CrSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> series, there is no significant change in the lattice volume of all phase pure tri-rutile samples, up to 30 % CrSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub>. However, when % of CrSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> has reached 40 % or above, secondary random rutile phase CrSbO<sub>4</sub> appears, refined lattice volumes of this secondary phase increases gradually until CrSbO<sub>4</sub> is completely formed, demonstrated in Figure 6.14. Other XSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> and NiSb<sub>2</sub>O<sub>6</sub> solid solutions where X= Al, Fe, In, and Nb show no changes in refined lattice parameters upon further analysis in Rietveld refinement, regardless of the peak shifts observed in some PXRD patterns, indicating that X did not successfully incorporate into the ZnSb<sub>2</sub>O<sub>6</sub> lattice.

In order to understand further the dependence of dopant size in the overall doping

mechanism, average ionic radii is taken into account, the average sum of the cation radii, namely Zn (0.74 Å) and Sb (0.60 Å) in the stoichiometric ratio of 1:2, is calculated to be 0.65 Å. Tri-valent cations, such as Ga and Cr, having similar and slightly smaller ionic radii, (0.62Å) to the average ionic radii, are more likely to substitute in the tri-rutile lattice. Having said that, Fe(III) have the same ionic radii (0.65 Å) as the average cation radii, yet the doping was unsuccessful possibly due to other underlying reasons such as the orbital arrangement in high spin Fe complexes. Other dopant ions, such as Al(III), In(III), Ni(II) and Nb(V), which have dissimilar ionic radii to 0.65 Å are less likely to incorporate in the tri-rutile lattice. In addition, Nb(V) has a 5+ oxidation state despite having an ionic radii of 0.64 Å. While both the oxidation state and size of ion are equally important factors in determining the doping outcome and mechanism, experimental results have shown that the oxidation state of a dopant ion.

As a result, only Ga(III) and Cr(III) are fully incorporated into the ZnSb<sub>2</sub>O<sub>6</sub> lattice and they are expected to exhibit n-type doping mechanism.



#### **Optical Spectroscopy**

Figure 6.15: Plots of (a) F(R) and (b)  $F(R)^2$  against energy of 0% and 100% GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> respectively.



Figure 6.16: Kubelka-transformed optical data and normalised F(R) values, which are proportional to absorption coefficients, of low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions.



Figure 6.17: Kubelka-transformed optical data and normalised F(R) values, which are proportional to absorption coefficients, of high % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions.



Figure 6.18: Band gap values of  $GaSbO_4$ : $ZnSb_2O_6$  solid solutions at different EDS measured composition of Ga.

Figure 6.16 shows that 4 % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solution has the highest charge carrier concentration amongst the low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions whereas GaSbO<sub>4</sub> has the highest charge carrier concentration in high% GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub>, with the assumption of optical constants being equal. This observation is coherent with the doping mechanisms described in the previous section where the main charge carriers, electrons, are produced when Ga dope into the ZnSb<sub>2</sub>O<sub>6</sub> lattice, replacing Zn. The possible change in electronic structure has also resulted in a higher charge carrier concentration in GaSbO<sub>4</sub>. The overall trend indicates that the absorption coefficient increases with wavelength because charge carrier absorption becomes significant at

longer wavelengths. For instance, 4 % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> compound has the highest charge carrier concentration, suggesting that it has some degree of conductivity. This phenomenon will be further discussed in the Electrical Conductivity section.

Figure 6.15 shows the plots of F(R) and  $F(R)^2$  where each of the absorption edges was extrapolated to the x-axis (y=0), giving values of  $E_1$  and  $E_2$  respectively. According to the Poeppelmeier method, the optical band gap value( $E_g$ ) can be calculated using  $2E_2 - E_1$ . All band gap values in Figure 6.18 were calculated using the above method.

All of GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions are wide band gap materials, with ZnSb<sub>2</sub>O<sub>6</sub> having a band gap of 3.54 eV, the band gap increases linearly with the amount of GaSbO<sub>4</sub> added due to the Burstein-Moss effect, resulting changes in the conduction band, symmetry and ordering of these solid solutions. Burstein-Moss effect stated that the majority charge carriers from dopant ion, electrons in this case, are constantly filling in additional energy levels in the conduction band, thus raising the Fermi level to a higher energy level in degenerate semiconductors. For this reason, all the solid solutions exhibit bigger optical band gap values than the expected increase between ZnSb<sub>2</sub>O<sub>6</sub> and GaSbO<sub>4</sub>. Apart from Burstein-Moss effect, these solid solutions are also expected to have different, or in this case bigger band gaps than the constituent materials, as ZnSb<sub>2</sub>O<sub>6</sub> and GaSbO<sub>4</sub> have dissimilar band gaps. Besides, the unprecedented changes in the electronic states of GaSbO<sub>4</sub> are accompanied by the change in lattice structure, site occupancies and electronic states: from an ordered tri-rutile to disordered random rutile; possible defects in the lattice; replacing Zn 2+ with Ga 3+. All of these result in the likelihood of a different electronic structure in GaSbO<sub>4</sub> compared to the other GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions. Thus, GaSbO<sub>4</sub> has a band gap of 3.90 eV, which is consistent with the value previously reported by Fu et al. 156 However, the origins of defects or potential changes in the electronic states are not very well understood, further work can be carried out to understand the correlation between charge carrier concentration and defects, and the associated changes in the electronic band structures.



Figure 6.19: Normalised absorption coefficient values between 280 nm to 1000 nm of CrSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions at different nominal composition of CrSbO<sub>4</sub> in  $ZnSb_2O_6$ .

Table 6.2: Optical band gap values of  $XSbO_4$ : $ZnSb_2O_6$  solid solutions where X= Cr, Al and Fe. Only phase pure compounds are included.

	Cr	AI	Fe	
	(eV)	(eV)	(eV)	
5%	3.99	4.09	4.11	
10%	4.00	4.05	4.18	
15%	3.89	4.06	-	
20%	3.89	-	-	

Table 6.3:	Optical	band ç	gap va	alues	of InS	bO₄:Zn	Sb <sub>2</sub> O <sub>6</sub>	solid	solutions.	Only	phase
pure comp	ounds ar	re inclu	ded.								

	In
	(eV)
2%	4.13
<b>4</b> %	4.12

CrSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions have so far behaved differently to the Ga series, they also exhibit different optical properties to Ga series. The peaks marked with an asterisk (\*) in Figure 6.19 indicate the d-d transitions and are consistent with the spinallowed d-orbital transitions obtained in Tanabe-Sugano diagram, namely  $t_{1{\it g}},\,t_{2{\it g}}$  and a<sub>2g</sub>.<sup>157</sup> As the lowest transition occurs at the lower detection limit of the machine, it cannot be easily distinguished from the optical data, yet the lowest transition is expected to occur in the series. Figure 6.19 also shows an initial band gap increase in  $\leq$ 10% CrSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions, after which there is no significant change in the band gap. However, accurate band gap values cannot be extracted from the optical spectra of high % CrSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions due to the increased absorption tail resulted from d-d transitions. Hence, the band gap values currently obtained are likely to be overestimates of the actual optical band gap values. Other series such as Al, Fe and In have seen much bigger band gap values than ZnSb<sub>2</sub>O<sub>6</sub>, possibly due to Burstein-Moss shift. Burstein-Moss shift occurs when the concentration of dopant ions increases, electron rich 3+ transition metal ions in this case, and reaches the point where electrons start to fill the energy states within the conduction band of the material, thus elevating the Fermi level above the conduction band minimum. As a result, electrons in the valence band can only be excited into energy levels above the Fermi level according to Pauli's exclusion principle and hence causing a shift in the optical band gap.



Figure 6.20: A plot showing all band gap values of various  $XSbO_4$ : $ZnSb_2O_6$  solid solutions where X= Cr, Al, Fe and In. Only phase pure compounds are being displayed.

All phase pure  $XSbO_4$ :ZnSb<sub>2</sub>O<sub>6</sub>, where X = Cr, Al, Fe and In solid solutions have bigger band gap values than ZnSbO<sub>6</sub> and show no further increase in band gap upon the addition of X, as illustrated in Figure 6.20. This is possibly due to the fact that electrons can no longer fill in the energy states any further in the conduction band of these solid solutions, likely to be accompanied by changes in symmetry and ordering in the lattice, these changes will also affect the conduction band structure.

### **Electrical Conductivity**



Figure 6.21: Electrical conductivities with associated error bars at different compositions of EDS measured % Ga at (a) 300 K and (b) 200 K.



Figure 6.22: Electrical conductivities with associated error bars at different compositions of EDS measured % Ga at (a) 100 K and (b) 65 K.

As-synthesised GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> powders samples with nominal composition of 2%, 8%, 10%, 15% and 20% GaSbO<sub>4</sub> were individually measured using Terahertz-Domain

Spectroscopy THz-TDS in order to obtain electrical conductivities. The complex conductivity values were obtained numerically and solved analytically via a mathematical model, which involves experimentally derived complex refractive indexes and dielectric functions. Due to the real and imaginary part of the refractive index being measured simultaneously in THz-TDS system, the complex conductivity can be understood in the form of  $\sigma = \sigma_1 + \iota \sigma^2$ .<sup>95,158</sup>

Figures 6.21 and 6.22 show that the conductivity increases from 0% Ga to 8% EDS measured compositions of Ga where it peaks and then decreases as there are more Ga in the GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions. The same observation occurs at lower temperatures, however, at 65 K, the uncertainty in measurements becomes more significant, causing the results to be slightly less reliable. Regardless, the overall conductivity of GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions are reduced at 65 K. Transparent-conducting oxides typically have decreased conductivity with temperature due to the charge carriers being less mobile at lower temperatures, this aligns well with the conductivity data.



Figure 6.23: Electrical conductivities with associated error bars at different compositions of XRF measured % Ga at (a) 300 K and (b) 200 K.



Figure 6.24: Electrical conductivities with associated error bars at different compositions of XRF measured % Ga at (a) 100 K and (b) 65 K.

As discussed previously, bulk composition measured by XRF demonstrate similar changes across all  $GaSbO_4$ :ZnSb<sub>2</sub>O<sub>6</sub> solid solutions compared to those obtained via EDS. Figure 6.23 and Figure 6.24 illustrate changes in conductivity with XRF measured composition of Ga and they display similar trends to that of EDS.

A transparent material can be a good electrical conductor when its plasma frequency, a characteristic frequency at which a material changes from being metallic to dielectric, is just below the visible frequencies. Because of this, results derived from THz-TDS experiment and optical measurements can be used to establish a correlation between conductivity and the reflectivity in GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions. All reflectivity values were obtained from Diffuse-Reflectance spectroscopy measurements.<sup>159,160</sup>

The Hagen-Rubens relation describes the relationship between the reflectivity and conductivity of a material and is valid for degenerate semiconductors below the plasma frequency, i.e. in the IR region.<sup>161</sup>

The Hagen-Rubens relation is known as

$$\mathcal{R}(\omega) \simeq 1 - 2\sqrt{\frac{m^*\omega}{2\pi n e^2 \tau}}$$

where  $\omega$  is the frequency, n is the total carrier density, e is the charge of an electron,  $\tau$  is the relaxation time of an electron between collisions and m<sup>\*</sup> is the electron effective mass.

$$\therefore \sigma = \frac{ne^2\tau}{m^*}$$
$$\therefore \mathcal{R}(\omega) \simeq 1 - 2\sqrt{\frac{\omega}{2\pi\sigma}}$$

Reflectivity of a material at a certain frequency  $\omega$  is inversely proportional to the square root of conductivity, assuming the dielectric constant is the same throughout the solid solution series.

$$\mathcal{R}(\omega) \sim \frac{1}{\sqrt{\sigma}}$$



Figure 6.25: Experimental reflectivity values plotted together with the conductivity values at different EDS measured % Ga.



Figure 6.26: Experimental reflectivity values plotted together with the conductivity values at different XRF measured % Ga.

In the previous section, optical measurements have demonstrated that there is charge carrier absorption in low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions and the likelihood of these compounds being conductive. The Hagen-Rubens relation allows a direct comparison between the conductivity and reflectivity of a material and is particularly useful in low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions. Figure 6.25 and Figure 6.26 show the changes in conductivity and reflectivity with EDS and XRF measured % Ga in GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions respectively, these changes in conductivity and reflectivity with % Ga are coherent with the Hagen-Rubens relation for degenerate semiconductors. This observation provides a clear insight and understanding into the electronic properties

of as-synthesised GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> materials, where Hall effect measurements would be difficult to perform otherwise.

A similar trend is expected in the band gap of low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions, however, a positive increment was observed in the band gaps of these compounds instead and displayed in Figure 6.18. Electrical conductivity increases as there are more charge carriers, electrons in this case, and it is expected that the conductivity should increase accordingly with the optical band gap values observed in these materials. The conductivity falls after 8 % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> as band gaps continue to increase, this phenomenon can be explained by the fact that conductivity is a product of the charge carrier concentration and mobility. In this situation, the charge carrier concentration increases steadily as more dopant is added to the solid solutions, yet the conductivity starts to decline after 8 % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub>, possibly due to a decrease in mobility, changes in the symmetry and ordering within the lattice. As a result, the structure of the conduction band would also change, in particular the curvature, symmetry and dispersity. Tri-rutile ZnSb<sub>2</sub>O<sub>6</sub> has a relatively disperse and symmetrical conduction band structure with high curvatures, it is possible that the conduction band becomes less disperse as ZnSb<sub>2</sub>O<sub>6</sub> gradually transforms into GaSbO<sub>4</sub>. The increase in disordering and random occupancy of Ga and Sb during this transformation would also likely induce changes in the orbital structure constituting the conduction band, thus lowering the charge carrier mobility, resulting in decreased conductivity.

## X-ray Photoelectron Spectroscopy



Figure 6.27: Surface composition of (a) Ga and (b) Sb and Zn at different nominal % of GaSbO4 in ZnSb2O6.



Figure 6.28: Valence band XPS spectra measured from 0 eV to 15 eV of GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions.

XPS spectra shown in Figure 6.27 indicate a similar change in Ga, Sb and Zn surface composition respectively in comparison to the bulk composition as mentioned in previous section across different nominal % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions. Surface composition of Ga increases whereas that of Sb and Zn decrease as more Ga is being added to the solid solution. Note that in high % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> compounds, there is more Sb segregated at the surface, which is commonly observed in Sb-rich compounds.

Valence band data were analysed with adjustments to adventitious C 1*s* at 284.8 eV, and measured amongst low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> series and GaSbO<sub>4</sub>. These were plotted in Figure 6.28. Two features are present in the valence band scan in these low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions. The first feature occurs at lower binding energy region between 3 eV to 5 eV while the second feature is observed in between 8 eV to 13 eV. There is a shift in both features as the % Ga increases in these solid solutions, the second feature occurring in higher binding energy region has shifted to a greater extent than the first feature. Additionally, the Fermi level is shifted further away from the valence band edge as the % Ga increases. The intensity of the second feature also decreases with increasing % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub>. For GaSbO<sub>4</sub>, only the first shoulder region can be seen in the valence band scan and the second feature is absent. These results suggest that all of these low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions exhibit n-type behaviour.

### **Thermoelectric Properties**

	Density
_	(%)
0%	67.3
<b>1</b> %	68.8
5%	64.2

Table 6.4: A table showing the densities of various GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> pellets used in thermoelectric measurements.

Thermoelectric properties including Seebeck coefficients, electrical conductivity, resistivity and power fraction were measured with our collaborators at University of Liverpool. Pellets of  $ZnSb_2O_6$ , 1% and 5% GaSbO<sub>4</sub>: $ZnSb_2O_6$  samples were measured in order to obtain initial results and thus compare their thermoelectric properties. Figure 6.29 shows the electrical conductivities of the samples from 300 K to 1000 K. Pellet of  $ZnSb_2O_6$  was measured once whereas pellets of 1% GasbO<sub>4</sub>: $ZnSb_2O_6$  were measured twice separately. However, during the measurement of 5% GasbO<sub>4</sub>: $ZnSb_2O_6$ sample, instrumental malfunction has halted the measurement between 700 K to 850 K. As a result, an alternative pellet made from the same batch of sample was used to carry out measurement at 850 K and beyond.



Figure 6.29: A graph showing the electrical conductivity of 0%, 1% and 5% GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions at a range of temperature from 300 K to 1000 K.



Figure 6.30: A graph showing the power fraction of 0%, 1% and 5% GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions at a range of temperature from 300 K to 1000 K.



Figure 6.31: A graph showing the resitivity of 0%, 1% and 5% GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions at a range of temperature from 300 K to 1000 K.



Figure 6.32: A graph showing the Seebeck Coefficient of 0%, 1% and 5% GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> solid solutions at a range of temperature from 300 K to 1000 K.

In Figure 6.29, the electrical conductivity of 5% GasbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> increases drastically above 500 K while ZnSb<sub>2</sub>O<sub>6</sub> shows a slightly increase and 1% GasbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> shows no increase at all. As the amount of Ga differs in only a very small amount between ZnSb<sub>2</sub>O<sub>6</sub> and 1% GasbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub>, it is possible that 1% GasbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> behaves similarly to ZnSb<sub>2</sub>O<sub>6</sub> and vice versa. It can be seen that the electrical conductivity generally increases with the amount of Ga in the solid solutions, suggesting that the addition of Ga in the system does improve the electrical conductivity. In previous research published by S. Nishiyama *et al.*, the electrical conductivity and Seebeck coefficient of ZnSb<sub>2</sub>O<sub>6</sub>.<sup>153</sup> The electrical conductivity was found to increase with increasing temperature, which is consistent to our data. In the paper, it was proposed that oxygen vacancies were present in ZnSb<sub>2</sub>O<sub>6</sub> synthesised in air and electrons were created as the main charge carriers in the system.

In order to assess other thermoelectric properties of these compounds, the power fraction, resistivity and Seebeck coefficient were measured and shown in Figure 6.30, 6.31 and 6.32 respectively.

Resistivity measures how well a material can conduct current as oppose to the electrical conductivity. As shown in 6.31, only 5 % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> sample has the highest resistivity at low temperature and slowly decreases at higher temperatures. Other samples such as ZnSb<sub>2</sub>O<sub>6</sub> and 1 % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> are shown to be non-resistive across the entire temperature range. Both ZnSb<sub>2</sub>O<sub>6</sub> and 5 % GasbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> samples have similar power fraction than 1 % GasbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub>, which are both much higher across the measured temperature range.

One of the crucial factors in determining the *zT* values of a thermoelectric material is the Seebeck coefficient, as mentioned previously in Chapter 1.3, it is often correlated to the charge carrier concentration of a material. However, materials with a large Seebeck coefficient often suffer from low charge carrier concentration and thus these materials usually have a relatively low electric conductivity. As such, Seebeck coefficient of a material is typically a compromise between all other factors such as electrical conductivity, lattice thermal conductivity, charge carrier concentration and temperature.

It was also proposed by S. Nishiyama et al. that the slope of Seebeck coefficient changes accordingly with the charge carrier concentration over a certain temperature range.<sup>153</sup> They found that the Seebeck coefficient of  $ZnSb_2O_6$  increased up to 330 K and beyond which, the slope decreased as temperature increased, suggesting that the charge carrier concentration decreased as temperature increased. This observation is coherent with our measured results of our as-synthesised  $ZnSb_2O_6$  sample, the slope of Seebeck coefficient, as demonstrated in Figure 6.32, increased up to 600 K and then decreases as temperature increases. The Seebeck coefficient of  $ZnSb_2O_6$  measured by S. Nishiyama is also in good agreement with our data, in which the Seebeck coefficient.

ficient values and changes across the same temperature range are very similar. The same study also suggested that when the Seebeck coefficients of all the samples measured, 1 % and 5 % GasbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub>, are less negative than that of ZnSb<sub>2</sub>O<sub>6</sub>, these compounds are likely to exhibit n-type semiconducting property.<sup>153</sup>

Regrettably the data obtained from thermoelectric measurements are not able to validate the thermoelectric properties of doped  $GaSbO_4$ : $ZnSb_2O_6$  solid solutions and thus it remains inconclusive as to whether % Ga has any effects upon the resistivity, electrical conductivity and Seebeck coefficient. Further study is required in order to establish a correlation between the amount of Ga in  $ZnSb_2O_6$  solid solutions and the corresponding thermoelectric properties.

### 6.4 Conclusion

We have doped  $ZnSb_2O_6$  with  $XSbO_4$  where X = Ga(III), Cr(III), AI(III), Fe(III), In(III),Ni(III) and Nb(V) and only in Ga(III) and Cr(III) a phase transformation from tri-rutile to random rutile is observed. The decrease in lattice volume in Ga series suggests Ga(III) are substituting on Zn(II) sites. Bulk EDS and XRF results are somewhat consistent with this observation, both datasets suggested the likelihood of an amorphous Zn-containing phase present in low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> compounds, however, these data are ambiguous and inconclusive as to whether Ga are precisely replacing Zn over Sb in the lattice. Though one can assume that Ga(III) are replacing mostly Zn sites in the tri-rutile structure over the Sb sites as indicated by theoretical calculations, it is also certain that Ga are also partially replacing Sb in the lattice. Moreover, the majority of these low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> compounds also display an increased charge carrier absorption in the near IR region of the optical spectra and the relative absorption coefficients decrease upon the addition of Ga, suggesting a significant presence of charge carriers. The increased charge carrier absorption aligns with the Kröger-Vink equation described in low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> compounds. In addition, band gap values of these low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> compounds increases non-linearly with the Ga content due to Burstein-Moss effect. On the other hand, high % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> compounds display a strong linear decrease in both Zn and Sb content, indicating that there is no preferential substitution of Ga(III) in the random rutile structure since both Zn and Sb sites are potentially crystalgraphic equivalent. The shift in the valence band XPS spectra evidently show that these low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> compounds are n-type semiconductors, and the change in the valence band features upon the addition of Ga in the lattice can be correlated to the change in the electronic structure, which can be shown via Time-Domain Terahertz Spectroscopy (THz-TDS) measurements. Electrical conductivity is measured via THz-TDS spectroscopy and low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> compounds displayed an increase in conductivity, in which 8 % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> has the highest measured conductivity, after which the conductivity decreases upon the addition of Ga in the system. This can be explained by the n-type semiconducting behaviour where electrons as the main charge carriers are created. It has also been demonstrated that these low % GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> compounds fulfil the Hagen-Rubens relation where the reflectivity is inversely correlated to the conductivity for a degenerate semiconductor. The overall changes in electrical conductivity over temperature is consistent with that of a typical TCO material where it decreases with temperature. In addition, thermoelectric results show negative values in Seebeck coefficients of all measured ZnSb<sub>2</sub>O<sub>6</sub> and GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> compounds, this is another indication that these compounds are highly likely to be n-type semiconductors. Unfortunately, the experimental results obtained from the thermoelectric measurements are not able to validate the thermoelectric properties of these GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> compounds as there seems to be a lack of consistency in the measurements. Repeated thermoelectric measurements can be carried out to validate the reproducibility and suitability of these compounds in thermoelectric applications.

CrSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> series have no significant change in lattice parameters up to 30 % and after which, phase separation into random rutile structure has made it difficult refining the main ZnSb<sub>2</sub>O<sub>6</sub> lattice. Bulk EDS and surface analysis have shown a gradual increase in Cr content and steady decrease in Zn content in the series, suggesting that Cr(III) are replacing Zn as expected and this substitution does not cause any changes to the tri-rutile and random rutile lattice. The band gap values are unable to be determined due to the presence of d-orbital transitions in these Cr-containing compounds, making it difficult to assert the potential applications of these compounds.

Amongst all the solid solutions, GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> is the most promising material to become a potential TCO and TE material due to its high band gap and thus high transparency, increased charge carrier absorption and reasonable electrical conductivity. Further work, however, is required to investigate the changes in electronic structure of these GaSbO<sub>4</sub>:ZnSb<sub>2</sub>O<sub>6</sub> and the corresponding electronic and thermoelectric properties.

## **Publications**

- Leung, WW Winnie; Savory, Christopher N; Palgrave, Robert G; Scanlon, David O, An experimental and theoretical study into NaSbS<sub>2</sub> as an emerging solar absorber, *J. Mater. Chem. C* 2019, *7*, 2059–2067.
- Karim, MS Karim; Ganose, Alex M; Pieters, Laura; Leung, WW Winnie; Wade, Jessica; Zhang, Lina; Scanlon, David O; Palgrave, Robert G, Anion Distribution, Structural Distortion, and Symmetry-Driven Optical Band Gap Bowing in Mixed Halide Cs<sub>2</sub>SnX<sub>6</sub> Vacancy Ordered Double Perovskites, *Chem. Mater.* **2019**, *31*, *22*, 9430–9444.

# **Pending Publications**

- Ganose, Alex M; Spooner, Kieran B; Leung, WW Winnie; Palgrave, Robert G; Scanlon, David O, BaBi<sub>2</sub>O<sub>6</sub> a promising n-type thermoelectric oxide with the PbSb<sub>2</sub>O<sub>6</sub> crystal structure.
- Leung, WW Winnie; Neu, Jens; Martin, Elizabeth; Schumuttenmaer, Charles A; Scanlon, David O; Palgrave, Robert G, Investigating the Cation-ordering and Electrical Conductivity in Tri-rutiles as Transparent Conducting Oxides.
- Jackson, Adam AJ; Ganose, Alex M; Leung, WW Winnie; Williamson, Benjamin AD; Kalra, Raman H; Palgrave, Robert G; Scanlon, David O, Doping Strategies for Transparent Conductor ZnSb<sub>2</sub>O<sub>6</sub>.
- Jackson, Adam AJ; Leung, WW Winnie; Ganose, Alex M; Godfrey, Ian J; Birkett Max; Veal, Tim D; Gopinathan, Sankar G; Palgrave, Robert G; Scanlon, David O, Hidden Structural Order in the New Transparent Conducting Oxide GaSbO<sub>4</sub>.
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