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The electronic structure of the antimony chalcogenide series: Prospects for optoelectronic applications

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Abstract

In this study, density functional theory is used to evaluate the electronic structure of the antimony chalcogenide series. Analysis of the electronic density of states and charge density shows that asymmetric density, or ‘lone pairs’, form on the Sb^{III} cations in the distorted oxide, sulphide and selenide materials. The asymmetric density progressively weakens down the series, due to the increase in energy of valence *p* states from O to Te, and is absent for Sb₂Te₃. The fundamental and optical band gaps were calculated and Sb₂O₃, Sb₂S₃ and Sb₂Se₃ have indirect band gaps, while Sb₂Te₃ was calculated to have a direct band gap at Γ . The band gaps are also seen to reduce from Sb₂O₃ to Sb₂Te₃. The optical band gap for Sb₂O₃ makes it a candidate as a transparent conducting oxide, while Sb₂S₃ and Sb₂Se₃ have suitable band gaps for thin film solar cell absorbers.

Key words: Antimony chalcogenides, DFT, electronic structure, asymmetric density, band gaps, solar cell absorbers.

1. Introduction

The antimony chalcogenides (Sb₂Ch₃, Ch = O, S, Se, Te) are of considerable interest for optoelectronic applications due to their high refractive indexes, photo-sensitivity, high electrical conductivity, strong adsorption and transport properties[1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14]. Antimony oxide (Sb₂O₃) is a potential candidate for photocatalysis due to its large and direct band gap located in the near-ultraviolet region[1, 2]. Sb₂O₃ is useful as a flame-retardant in polymers, adhesives and textile back coatings[15, 16, 17]. Antimony sulphide (Sb₂S₃) has potential applications in solar energy conversion[11], thermoelectrics and optoelectronics[10, 12] while antimony selenide (Sb₂Se₃), a high refractive material, is used for optical coatings in thermophotovoltaic applications[18], optical storage and photovoltaic conversion[19]. Antimony telluride (Sb₂Te₃) is mainly used as a thermoelectric

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material[20, 21, 22, 23] and has recently been identified as a topological insulator (TI), which contains an insulating bulk band gap and gapless metallic surface conductivity[24, 25].

The Sb_2O_3 structure exists in three different polymorphs (α , β and γ) with each being distorted from the presence of lone pairs on the Sb^{III} cations[26]. The focus of previous studies for Sb_2O_3 has been the electrical, vibrational and optical properties[6, 7, 27, 28, 29]. Optical band gaps in the range of 3.40-4.00 eV have been reported for Sb_2O_3 , with the indirect/direct nature of the band gap unclear[6, 7, 28]. Hartree-fock calculations were used to characterise the electronic density of the Sb_4O_6 clusters in the Senarmontite structure, indicating the presence of lone pairs on the Sb cations[30]. The ground state vibrational frequencies and molecular orbitals were deduced using second order Møller-Plesset and density functional theory (DFT) using the B3LYP exchange correlation functional[27]; however, there was no examination of lone pairs or band structure analysis. A DFT study by Matsumoto *et al.*[31] using the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional based on the generalised gradient approximation (GGA), examined the ground state electronic structure of Sb_2O_3 , along with As_2O_3 and Bi_2O_3 . The electronic band structure for Sb_2O_3 was examined, calculating a fundamental band gap of 3.33 eV; however, neither the direct/indirect nature of the fundamental band gap or optical adsorption was investigated. Band structure calculations for Sb_2S_3 using PBE-DFT show that it possesses an indirect fundamental band gap of 1.35 eV with the valence band maximum and conduction band minimum located at G and Y, respectively[32]. Sb_2S_3 has a direct optical band gap with experimental studies reporting a range from 1.66-2.24 eV[14, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41], which is found to increase with the film thickness and temperature[42, 43]. The nature of the band gap for Sb_2Se_3 is also unclear but an experimental range of 1.00-1.82 eV has been reported, where the lower energy transitions are considered to be indirect[44, 45, 46, 47]. A PBE study by Vadapoo *et al.*[48] calculated an indirect band gap of 0.88 eV for Sb_2Se_3 ; however this is likely to be an underestimated value which is often the case when using a GGA functional like PBE. The optical band gap for Sb_2Te_3 has been investigated experimentally with values between 0.29 eV and 0.46 eV depending on film thickness[49, 50]; however the indirect/direct nature of the transitions was not ascertained. For Sb_2Te_3 , theoretical studies have focused on explaining the thermoelectric properties and the effect of uniaxial pressure on its band structure[20, 21, 51, 52]. The calculated band structure of Sb_2Te_3 is in contention as some reports have shown that it is a direct band gap material at Γ (0.14 eV)[53], while others have indicated that its VBM and CBM are off set from the high symmetry points in the Z-F and Γ -Z directions, respectively, with a band gap of 0.28 eV[20, 21, 54]. Thonhauser *et al.*[52] suggested that this discrepancy is a result of the presence or absence of spin orbit coupling (SOC) with the VBM located in the Z-F direction with SOC and at Γ without; however, Park *et al.*[23] suggested that the difference in the position of the VBM/CBM is related to the change in the volume of the relaxed cell with SOC leading to a reduction in the volume relative to PBE.

The atomic structures of antimony oxide, sulphide and selenide are all distorted, while the telluride adopts a highly symmetric hexagonal structure. The crystal distortion and stabilisation of these materials is typically explained by the presence of Sb^{III} ‘lone pairs’[26,

30]. The electronic structure of the Sb^{III} cation is $[\text{Kr}] 4d^{10} 5s^2 5p^0$, where the $5s$ electrons are thought to form a chemically inactive sp hybridised lone pair[55, 56] which is sterically active, resulting in a distorted coordination environment for the Sb^{III} cation. The same argument, however, would also predict Sb_2Te_3 to possess a distorted structure. The lack of distortion suggests that the role of lone pairs in these crystal structures is more complicated than previously described.

The inert pair effect[57] was originally challenged by Watson and Parker using DFT and the PW91 functional to calculate the electronic structure of $\alpha\text{-PbO}$ [58, 59]. They showed that the classical sp hybrid orbital cannot form as the energy gap between the $6s$ and $6p$ orbitals is too large. The distorted $\alpha\text{-PbO}$ structure was found to arise from the stabilisation of the anti-bonding $\text{Pb}^{(6s)}\text{-O}^{(2p)}$ interaction at the top of the valence band by the $\text{Pb } 6p$ states. This theory was later supported by experimental studies[60, 61].

As the formation of the lone pair was found to be dependent on the interaction of the cation with the $\text{O } 2p$ states, the effect of changing the anion on the lone pair was further investigated by Walsh and Watson for PbO and PbS and the Sn monochalcogenide series[62, 63]. From PbO to PbS , as well as moving down the Sn monochalcogenides, the structure progresses from a distorted litharge structure to the symmetric rocksalt motif. In both instances, the distorted structures are found to contain asymmetric charge density (lone pairs) on the cations, which are absent in the symmetric structures. The change in lone pair activity was shown to be a result of the energy gap between the cation s states and anion p states increasing from the oxide ($2p$) to the telluride ($5p$). The revised model has since been extended to other lone pair materials such as SnO [64, 65], Bi_2O_3 [66], $\text{Bi}_2\text{Sn}_2\text{O}_7$ [67], Pb_2MgWO_6 [68], BiMnO_3 [69], BiOF , $\text{Bi}_2\text{Ti}_2\text{O}_7$ [70], and $\text{Bi}_2\text{Tc}_2\text{O}_{7-\delta}$ [71]. A recent study by Matsumoto *et al.*[31] supported the role of the anion in the formation of the lone pairs, and the stabilisation of the Sb_2O_3 , As_2O_3 and Bi_2O_3 distorted structures.

The formation of lone pairs in such materials leads to a mixed valence band of metal s/p and anion p states. The extent of mixing between the metal s and anion p states creates a dispersed valence band with the VBM raised through the anti-bonding nature of the interactions. This can reduce the band gap and has become an important concept in band gap engineering and is used to design devices with tailored band gaps for optoelectronic applications[72, 73, 74, 75]. Additionally, the valence band mixing of metal s with anion p states suggests that materials with lone pairs on the cations may be good candidates for p -type conducting materials[76, 77, 78, 79]. As the Sb^{III} cations are expected to possess lone pairs for the distorted systems, this may indicate that they could be potential candidates for p -type conducting materials. Furthermore, altering the anion from O to Se may reduce the band gap and improve their properties for optoelectronic devices[7, 12].

As previous studies[30, 36] have attributed the lone pair formation to the classical sp hybrid orbital description, rather than a stabilisation of $\text{Sb-}Ch$ antibonding orbitals, the electronic structure of the antimony chalcogenides will need to be re-examined as described by the revised model[58]. This study will thus examine the electronic structure of the antimony chalcogenide series using DFT calculations employing the PBE functional. Electronic density of states (EDOS), partial (ion and l -quantum number decomposed) density of states

(PEDOS) and charge density plots are used to provide a full characterisation of the Sb_2Ch_3 bonding characteristics, identifying any trends across the series.

2. Theory/calculation

Periodic-DFT was used through the VASP code[80, 81] with a plane wave basis set. The interactions between the core (Sb:[Kr] $4d^{10}$, O:[He], S:[Ne], Se:[Ar] $3d^{10}$, Te:[Kr] $4d^{10}$) and valence electrons were described using the projector-augmented wave (PAW) approach[82]. All calculations were performed using the PBE[83] exchange-correlation functional.

Optimisation of the structures was performed through a series of constant volume calculations, where the lattice vectors, angles and atomic positions were allowed to relax while the cell volume was kept constant. The energies obtained were fitted to the Murnaghan equation of state[84] to find the minimum energy volume. This approach minimises potential problems of Pulay stress and changes in basis set which can accompany volume changes in plane wave calculations. Although the Pulay stress can be anisotropic, this method has been shown to be accurate by comparing the pressure along different lattice vectors for the SnO structure with 500 eV and 1000 eV cut-offs[85]. Primitive cells were used for each system and the structures were deemed converged when the force on each ion was less than 0.01 eV/Å. An energy cut-off parameter of 500 eV and a Monkhorst-Pack[86] k -point sampling grid of $6 \times 6 \times 6$ for Sb_2O_3 , $2 \times 12 \times 2$ for Sb_2S_3 , $2 \times 2 \times 12$ for Sb_2Se_3 and $6 \times 6 \times 2$ for Sb_2Te_3 was sufficient for convergence. To calculate the PEDOS, the wavefunctions were projected onto spherical harmonics centred on each atom with a radius of 1.45, 1.55, 1.88, 2.05, 2.07 Å for Sb, O, S, Se and Te, respectively. For Sb_2Se_3 and Sb_2Te_3 , spin-orbit coupling was included to assess its effect on orbital contributions to the top of the valence band (VB) and the bottom of the conduction band (CB), since this is required for DFT studies of TIs.[87]

The optical absorption spectra and the optical transition matrices were calculated within the transversal approximation[88]. The Tauc relation states that for a direct allowed transition, the optical band gap of a material can be obtained by plotting $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating $(\alpha h\nu)^2$ to zero, as described previously[89]. This approach sums all direct VB to CB transitions on the k -point grid but does not take into account indirect and intraband transitions[90]. Single-particle transitions are only considered, thus electron-hole correlations are not treated and would require higher order electronic structure methods[91, 92, 93]. The approach has been shown to provide reasonable optical absorption spectra in comparison to experiment[94, 95, 96, 97, 89].

The structures and charge density plots are generated using the VESTA visualisation package[98].

3. Results

3.1. Sb_2O_3

Antimony oxide crystallises in three primary polymorphs, a low temperature cubic phase, Senarmontite (α - Sb_2O_3), a high temperature orthorhombic phase, valentinite (β - Sb_2O_3), and a high temperature phase, γ - Sb_2O_3 [26, 30]. Of these three structures, the cubic α phase is of

particular interest since it is the most thermodynamically stable at standard conditions[5]. The structure of α - Sb_2O_3 (space group $Fd\bar{3}m$), shown in Figure 1, is comprised of discrete Sb_4O_6 molecular units. The Sb_4O_6 sub-units contain bridging oxygen atoms with each antimony bonded to three oxygens. The Sb cations have a tetrahedron arrangement, with three oxygen atoms forming the base and the fourth vertex, which faces away from the cluster, vacant. All bond lengths in the Sb_4O_6 unit are equivalent and the molecular units are held together by non-bonding dispersion interactions.

Figure 1: The unit cell of α - Sb_2O_3 , with an Sb_4O_6 cluster in the inset. The purple spheres are the Sb cations and the red spheres are the O anions.

The calculated lattice vectors and bond lengths are detailed in Table 1, with the lattice vectors deviating from experiment more than expected for a PBE calculation. Despite this expansion, the calculated bond lengths are in better agreement with experiment, implying that the bonding between the Sb-O atoms is likely to be reproduced well. The main cause of the lattice expansion is the failure of DFT to correctly model the presence of non-bonding dispersion interactions between the Sb_4O_6 sub units. This is unsurprising as standard functionals are known to fail to describe dispersion forces[99] without some form of correction[85, 100, 101, 102].

Property	Calculated
a	11.537 (+3.8%)
Volume	1535.720 (+11.8%)
Sb - O	2.008 (+1.5%)

Table 1: The optimised cell vectors, volume and bond distance, for the Sb_2O_3 . The percentage difference to experimental value[26] are shown in the parentheses and all values are in Å, except cell volume which has units of Å³.

To analyse the bonding characteristics between Sb^{III} cations and the O anions in the α - Sb_2O_3 structure, the EDOS and PEDOS are shown in Figure 2. The PEDOS is split into four distinct regions for clearer analysis. Region I is a mixture of Sb 5s and O 2p with the majority from Sb 5s while region II is a mixture of Sb 5s/p and O 2p states. Region III contains a major contribution from O 2p states, mixed with Sb 5s and 5p states. The bottom of the conduction band (region IV) is a mixture of Sb 5p states with a smaller

contribution of O $2s/p$ states. The regions of interest are region I and the top of the valence band (region III) which are composed of the Sb-O bonding and anti-bonding interactions, respectively[63]. The presence of Sb $5p$ states in this region stabilises the Sb-O anti-bonding interaction, which is characteristic of lone pair materials[58, 59, 62, 63]. The charge density associated with region III is shown in Figure 2. The charge density plot shows the formation of asymmetric density on the Sb cations from the antibonding mixing of states in this region.

Figure 2: The calculated EDOS and PEDOS of α - Sb_2O_3 with the partial charge density shown for region III. The top of the valence band is set to 0 eV as indicated by the black dashed line. The s , p and d states are coloured blue, red and green respectively. The charge density plot of region III ranges from 0 (blue) to 0.15 electrons/ $\text{\AA}^3$ (red).

The band structure for α - Sb_2O_3 , calculated along high symmetry lines[103], is shown in Figure 3(a). The VBM is located at the L point and the conduction band minimum (CBM) is at Γ . The fundamental band gap was calculated to be 3.38 eV and it is indirect in nature, with the smallest direct gap (3.54 eV) located offset from X in the Γ direction. The calculated fundamental indirect band gap is in good agreement with a previous PBE study, which reported a value of 3.33 eV, although they did not comment on whether it was direct or indirect[31].

The calculated optical absorption spectrum for α - Sb_2O_3 is plotted in Figure 3(b). The optical band gap for α - Sb_2O_3 is determined to be 3.54 eV, with the onset of optical absorption occurring at the smallest direct fundamental gap. The experimental optical band gap of α - Sb_2O_3 has been reported to be in the range of 3.4-4.0 eV, depending on film thickness[6, 7], as well as being direct in nature[7]. In contrast, an early optical study reported an optical band gap of approximately 4.0 eV resulting from indirect transitions[1]. The calculated optical band gap in this study is in good agreement with the low end of the experimental range, consistent with the PBE functional (and other GGA functionals) underestimating

band gaps[104].

Figure 3: The calculated (a) band structure and (b) optical absorption spectra $(\alpha h\nu)^2$ for α - Sb_2O_3 . The VBM is set to 0 eV, as indicated by the red dashed line.

3.2. Sb_2S_3

Antimony sulphide crystallises in an orthorhombic structure with space group $Pnma$, as shown in Figure 4. Sb_2S_3 is a layered structure with molecular ribbons which are held together by non bonded interactions. The Sb^{III} cations reside in two different coordination environments, labelled Sb_1 and Sb_2 . The Sb_1 cation is coordinated to five S anions, while the Sb_2 cation is coordinated to six S anions.

Figure 4: The unit cell of Sb_2S_3 . The purple spheres are the Sb cations and the yellow spheres are the S anions.

The calculated cell vectors, volume and bond lengths are detailed in Table 2. The lattice vectors in the b and c directions are observed to be in good agreement with the experimental parameters. The a vector, however, shows a larger deviation. The calculated bond lengths are also in good agreement with experiment, with errors typical of PBE calculations. As

the bond lengths are in good agreement with experimental data, the overestimation of the a vector and cell volume is due to the presence of non-bonded interactions between the Sb_2S_3 ribbons. Despite this error, the reasonable bond lengths indicate that the electronic structure is likely to be well reproduced.

Property	Calculated
a	12.150 (+7.7%)
b	3.870 (+1.0%)
c	11.270 (+0.4%)
Volume	529.92 (+9.3%)
$\text{Sb}_1 - \text{S}_1$	2.482 (+1.3%)
$\text{Sb}_1 - \text{S}_2$ (x2)	2.695 (+0.7%)
$\text{Sb}_1 - \text{S}_3$ (x2)	2.870 (+0.7%)
$\text{Sb}_2 - \text{S}_1$ (x2)	3.149 (+1.4%)
$\text{Sb}_2 - \text{S}_2$	2.548 (+1.3%)
$\text{Sb}_2 - \text{S}_3$	3.233 (+2.2%)
$\text{Sb}_2 - \text{S}_4$ (x2)	2.568 (+1.2%)

Table 2: The optimised cell vectors, volume and bond distances, for the Sb_2S_3 . The percentage difference to experimental values are shown in the parentheses[105].

The calculated EDOS and PEDOS for Sb_2S_3 is shown in Figure 5, and partitioned in a similar manner to that of $\alpha\text{-Sb}_2\text{O}_3$. Region I contains a large contribution from the Sb 5s states, mixing with S 3p states, while region III is comprised mainly of S 3p states mixing with Sb 5s and 5p states. This mixing at the top of the VB would suggest the formation of lone pairs on the Sb^{III} cations in the Sb_2S_3 structure. To confirm this, the charge density for region III is shown in Figure 5. This shows the characteristic asymmetric density on the Sb^{III} cations of the anti-bonding region; however its formation is not as strong as for $\alpha\text{-Sb}_2\text{O}_3$, indicating a weaker interaction between Sb cations and S anions in line with the *SnCh* series[63, 106].

The band structure calculated for Sb_2S_3 is shown in Figure 6(a). The VBM is located offset from point Y towards T and the CBM is located offset from point Z in the Γ direction. This gives an indirect fundamental band gap of 1.29 eV with the smallest direct gap (1.36 eV) located offset from Z in the Γ direction. This results in similar values to previous PBE calculations[32] which found an indirect gap of 1.35 eV and local density approximation (LDA) calculations[36] reporting a band gap of 1.55 eV, although the nature of the gap was not stated. GGA calculations using the Engel-Vosko functional[107], however, reported a much larger direct band gap of 1.76 eV, albeit this was based on a limited set of k -points. The calculated band structure is in closer agreement with a previous PBE study[32]; however, their reported VBM and CBM are located at Γ and Y, respectively, which are different to this study since they did not fully explore the brillouin zone.

The calculated optical absorption for Sb_2S_3 is plotted in Figure 6(b). The optical band gap was calculated to be 1.40 eV with transitions located around the smallest direct gap,

Figure 5: The calculated EDOS and PEDOS of Sb_2S_3 with the partial charge density shown for region III. The top of the valence band is set to 0 eV, as indicated by the black dashed line. The s , p and d states are coloured blue, red and green respectively. The charge density plot of region III ranges from 0 (blue) to 0.15 electrons/ $\text{\AA}$ (red).

at the Z point from the top of the VB to the CBM. The calculated optical band gap is underestimated compared to the experimentally reported range of 1.67-2.24 eV[12, 14, 33, 34, 37, 38, 39, 41].

3.3. Sb_2Se_3

Spin-orbit coupling (SOC), has been shown to be necessary for correctly describing the electronic structure of TIs such as Bi_2Se_3 , Bi_2Te_3 and Sb_2Te_3 [24, 52]. TIs are characterised by topologically protected metallic surface states with an insulating bulk gap. The topological surface states at the band edges are protected by time-reversal symmetry, and differ from those in the quantum hall effect due to the locking of their electronic spin and momentum[108]. Time reversal symmetry results in an inversion between the cation and anion p states at the VBM and CBM[24] where the cation p states are observed to be lower in energy than the anion p states. For this reason the inclusion of SOC has been indicated by experiment and theory to be important to correctly describe their electronic structure[109].

To assess the need for SOC when modelling Sb_2Se_3 , the Sb and Se p contributions to the VBM and CBM were analysed for PBE (Figure 7 a) and PBE with SOC (Figure 7 b). The inclusion of SOC increases the cell volume by 0.6% which is negligible. Figure 7 shows that for both approaches the CBM is dominated by Sb p states (Figure 7(i)) while the VBM is dominated by Se p states (Figure 7(ii)), indicating that no inversion takes place and PBE is a suitable approach to model Sb_2Se_3 , as suggested by a previous theoretical study[24].

Antimony selenide crystallises in the same layered orthorhombic structure to Sb_2S_3 , shown in Figure 4. Table 2 details the cell vectors and volume for the Sb_2Se_3 system with

Figure 6: The calculated (a) band structure and (b) optical absorption spectra $(\alpha h\nu)^2$ of Sb_2S_3 . The VBM is set to 0 eV, as indicated by the red dashed line.

Figure 7: The calculated (a) GGA and (b) GGA-SOC band structures of Sb_2Se_3 between Γ -Y. The band structures are shown in a fatband format with the contribution to the bands from (i) Sb p and (ii) Se p states. The top of the VB is set to 0 eV as indicated by the black dashed line.

comparison to experimental values. The a and c vectors are in good agreement with experiment; however, the a vector is overestimated for similar reasons to Sb_2S_3 .

The EDOS and PEDOS for the Sb_2Se_3 system is shown in Figure 8, which is similar to Sb_2S_3 with region I representing the Sb-S bonding interactions. The top of the VB (region III) is comprised of Sb $5s/p$ with a contribution from the Se $4p$ states. The asymmetric density associated with the anti-bonding region III is shown in Figure 8, weaker than Sb_2S_3 .

The calculated band structure is shown in Figure 9(a). The VBM is offset from Γ towards Y while the CBM is offset from Y towards Γ with an indirect fundamental band gap of 0.75 eV. The smallest direct gap is 0.78 eV and located offset from Γ in the direction of Y. The calculated fundamental band gap is in good agreement with previous PBE studies that report an indirect band gap of 0.88 eV and 1.21 eV with G_0W_0 corrections[48, 111]. A LDA study reported a band gap of 1.14 eV, but they did not comment on its nature[36]. A PBE-DFT study determined the VBM and CBM to be located between U-Y and Γ -X, respectively[48]. However, they did not consider the direction Γ -Y which was found to contain the VBM and CBM in this study. Our calculated VBM is 0.2 eV lower in energy

Property	Calculated
a	12.846 (+9.4%)
b	4.033 (+2.0%)
c	11.544 (-0.4%)
Volume	598.07 (+11.1%)
Sb ₁ - Se ₁	2.622 (+1.6%)
Sb ₁ - Se ₂ (x2)	2.822 (+1.2%)
Sb ₁ - Se ₃ (x2)	3.037 (+1.8%)
Sb ₂ - Se ₁ (x2)	3.234 (+1.2%)
Sb ₂ - Se ₂	2.707 (2.2%)
Sb ₂ - Se ₃	3.266 (+1.0%)
Sb ₂ - Se ₄ (x2)	2.718 (+2.2%)

Table 3: The optimised cell vectors (Å), volume (Å³) and bond distances (Å), for the Sb₂Se₃. The percentage difference to experimental values[110] are shown in the parentheses.

than the minimum found along the Γ -X direction.

The calculated optical adsorption for Sb₂Se₃ is plotted in Figure 9(b) with the onset originating at transitions located around the smallest direct gap. The calculated optical band gap is underestimated compared to the lowest value for the experimental range (1.00-2.14 eV) as a consequence of the underestimated band gap[48].

3.4. Sb₂Te₃

Antimony telluride has recently been shown to be a TI[24, 25]. The requirement for SOC was thus tested in a similar manner to Sb₂Se₃. The contribution of the Sb and Te p states to the VBM/CBM was analysed along the F- Γ -L direction, and is shown in Figure 10. This illustrates that without SOC the Sb p states dominate the CB and the Te p states dominate the VB. The inclusion of SOC shows that inversion occurs where Sb p states appear at the VBM and a larger contribution of Te p states at the CBM, as shown experimentally[24]. SOC is therefore required to correctly model the electronic structure of Sb₂Te₃, thus the cell was optimised and analysed with the inclusion of SOC.

The Sb₂Te₃ unit cell is shown in Figure 11, which possesses a layered hexagonal structure with space group $R\bar{3}m$ [112]. The Sb₂Te₃ layers are held together by dispersion interactions in the c direction and the Sb^{III} cations are fully coordinated in a distorted octahedral geometry to Te anions in two different environments. The two different Te sites exist at the edge of the layers (Te1) and within the layers (Te2) (Figure 11).

The calculated lattice vectors, volume and bond lengths for Sb₂Te₃ are detailed in Table 4 with comparison to experimental values. The a vector, along with the bond lengths, are in close agreement with experiment. The c vector is over estimated to a greater extent due to the non-bonding interactions in this direction.

The calculated EDOS and PEDOS for Sb₂Te₃ is shown in Figure 12. Region I contains a large contribution of Sb 5s states with smaller contributions from Te 5s/ p . The top

Figure 8: The calculated EDOS and PEDOS of Sb_2Se_3 with the partial charge density shown for region III. The top of the valence band is set to 0 eV as indicated by the black dashed line. The s , p and d states are coloured blue, red and green respectively. The partial charge density plot of region III ranges from 0 (blue) to 0.15 electrons/ $\text{\AA}^3$ (red).

Property	Sb_2Te_3
a	4.352 (+2.0%)
c	31.538 (+3.5%)
Volume	597.327 (+7.9%)
Sb - Te_1	3.038 (+1.9%)
Sb - Te_2	3.209 (+1.3%)

Table 4: The optimised cell vectors ($\text{\AA}$), volume ($\text{\AA}^3$) and bond distances ($\text{\AA}$), for Sb_2Te_3 with GGA+SOC. The percentage difference to experimental values are shown in parenthesis[112].

of the VB, region III, contains a mixture of Sb 5s states with Te 5p states and a minor contribution of Sb 5p states. The degree of mixing of the Sb 5s/p states with the Te 5p states has diminished compared to the other Sb_2Ch_3 materials.

The charge density associated with region III is shown in Figure 12, with the plot showing the absence of asymmetric density on the Sb^{III} cations while the majority of the electron density resides on the Te anions. The absence of asymmetric density on the Sb^{III} cations is due to the Sb cations being fully coordinated by Te anions and no distortions are present to allow lone pair formation.

The calculated band structure for Sb_2Te_3 is shown in Figure 13(a). The fundamental band gap was calculated to be 0.09 eV and it is direct in nature, with the VBM and CBM both located at the Γ -point similar to a previous GGA study[53]. The location of the VBM/CBM and nature of the band structure does not change with the inclusion of SOC as suggested

Figure 9: The calculated (a) band structure and (b) optical absorption spectra $(\alpha\hbar\nu)^2$ for Sb_2Se_3 . The VBM is set to 0 eV, as indicated by the red dashed line.

previously[52]. The band structure of the experimental structure was also calculated without allowing the lattice to relax, finding an indirect band gap with the VBM and CBM located between the Z-F and Γ -Z directions, respectively, similar to previous studies[20, 21, 54]. The relaxed GGA-SOC band structure (Figure 13) in this study contains a peak at the top of the VB in the Z-F direction; however this is 0.02 eV lower in energy than the VBM at Γ . The location of VBM and CBM at Γ , and the direct nature of the band gap, are consequences of the over expansion of the c vector (3.5%). These results show that the volume expansion of the cell has a small effect on the band energies and hence on the position of the band edges as suggested previously[23].

The optical gap for Sb_2Te_3 was also calculated to be 0.09 eV, resulting from the transition between the VBM to the CBM at the Γ point. The calculated value is less than the lowest reported value in the experimental range from 0.29 to 0.46 eV[49, 50]. This deviation can be attributed to underestimation of band gaps by PBE.

4. Discussion

In this work, the electronic structures of the antimony chalcogenide series were calculated using a PBE-DFT approach. Although, the lattice vectors that are strongly influenced by non-bonding dispersion interactions are over estimated with PBE calculations, the bonded interactions are in good agreement with experiment (within 2%).

The distortions present in the layered oxide, sulphide and selenide materials have been attributed to the presence of lone pairs[26, 30]. Charge density analysis of the top of the VB (region III) reveals that asymmetric density is centred on the Sb cations for the distorted structures (Sb_2O_3 , Sb_2S_3 , Sb_2Se_3) and absent on the Sb cations in the Sb_2Te_3 material. The asymmetric density is found to be a consequence of the anti-bonding Sb s - Ch p combination at the top of the VB, which requires a distortion so that the Sb $5p$ states can stabilise this interaction. The PEDOS show that this region consists of Sb $5s/p$ mixed with the anion p states. The mixing between the Sb $5s/p$ states and chalcogenide p states, along with the change in energy of the chalcogenide p states down the series is schematically illustrated in

Figure 10: The calculated (a) GGA and (b) GGA-SOC band structure of Sb_2Te_3 along the F- Γ -L direction. The band structures are shown in a fatband format with the contribution to the bands from (i) Sb p and (ii) Te p states.

Figure 11: The unit cell structure of Sb_2Te_3 . The purple spheres are the Sb cations and the grey spheres are the Te anions.

Figure 14. It can be seen that the energy gap of the Sb $5s$ - Ch p anti-bonding combination reduces down the series due to the change in energy of the Ch p states from O $2p$ to Se $4p$. The Sb $5s$ contribution to the top of the VB reduces down the series, which reduces the potential stabilisation by mixing with the Sb $5p$ states. The energy gap between Sb $5s$ and Te $5p$ states becomes large enough that the Sb $5s$ contribution to the anti-bonding states becomes small. This results in a reduced mixing with the Sb $5p$ states, and hence weakens the stabilisation of the anti-bonding states, which can therefore not compensate for the lower coordination of an asymmetric structure. Sb_2Te_3 thus takes on a symmetric structure and the Sb $5p$ do not mix with the states at the top of the VB. The results of the Sb chalcogenide series are in support of previous studies of the revised lone pair model[58, 59, 60, 62, 63, 64, 113]. A similar reduction in lone pair activity from O to Te was observed previously for the Sn monochalcogenide series and from PbO to PbS[62].

The oxide, sulphide and selenide were all found to possess fundamental indirect band gaps

Figure 12: The calculated GGA+SOC EDOS and PEDOS of Sb_2Te_3 and the charge density shown for region III. The top of the valence band is set to 0 eV as indicated by the black dashed line. The s , p and d states are coloured blue, red and green respectively. The partial charge density plot ranges from 0 (blue) to 0.15 electrons/ $\text{\AA}^3$ (red).

with their lowest energy transitions occurring at the smallest direct band, while the telluride was found to have a direct band gap at Γ . The fundamental and optical band gaps of the chalcogenide series are observed to decrease down the series from Sb_2O_3 to Sb_2Te_3 . This can be attributed to the increased energy of the Ch p states down the series pushing up the VBM, and thus, decreasing the band gap between the Sb $5p$ at the bottom of the CB and the Sb s - Ch p anti-bonding states at the top of the VB. The size of the fundamental and optical band gaps are therefore, dependent on the Sb s - Ch p anti-bonding interaction and the degree of mixing of states at the VBM, which effects the photo-physical properties of these and other similar lone pair materials.

Sb_2O_3 has a calculated fundamental and optical band gap greater than 3.1 eV making it a potential transparent conducting oxide with hole and electronic effective masses of 2.57 and 0.85, respectively[114]. The fundamental band gap of the antimony sulphide (1.29 eV), and selenide (0.75 eV) are indirect in nature, albeit underestimated by PBE, with their smallest direct gap being 1.36 eV and 0.78 eV, respectively. The optical transitions are found to occur at the smallest direct gap which are likely to fall within the optimum range for solar cell absorbers, which will ideally have a direct band gap in between 0.9 to 1.8 eV[115]. Currently crystalline Si (c-Si) is used as a solar cell absorber with an indirect band gap of ~ 1.1 eV and a direct gap of ~ 3.2 eV[116]. Alternatives such as CuInS_2 (1.53 eV), CuInSe_2 (1.00 eV) and CdTe (1.5 eV) are ideal candidates, albeit highly expensive. Sb_2S_3 and Sb_2Se_3 can be considered as suitable alternative candidates to Cu based materials and c-Si, as there is a small difference between the indirect fundamental and smallest direct band gaps (0.07 and 0.03 for the sulphide and selenide, respectively) indicating that these materials should be

Figure 13: (a) The calculated band structure of Sb_2Te_3 with SOC. The VBM is set to 0 eV, as indicated by the red dashed line. The calculated optical absorption spectra $(\alpha h\nu)^2$ for Sb_2Te_3 is given in (b).

more efficient than c-Si for thin film solar cell devices.

5. Conclusion

This study has used density functional theory with the PBE functional to model the electronic structure of the antimony chalcogenide series. The bond lengths of the relaxed structures are in good agreement with experiment, indicating that the electronic structure is reproduced well. The change from a highly distorted Sb_2O_3 structure to the hexagonal symmetric Sb_2Te_3 structure can be explained by the formation of asymmetric density or lone pairs, on the Sb^{III} cations. The lone pair formation is a result of the stabilisation of the Sb 5s-anion p anti-bonding states by the Sb 5p states at the top of the VB, similar to other lone pair materials[58, 59, 60, 62, 64, 113]. The asymmetric density on the Sb^{III} cations weakens down the series due to the increase in energy gap between the Sb 5s and Ch p states, as also observed for the Sn monochalcogenide series[63]. The increased energy gap between the Sb 5s Ch p states down the series progressively decreases the fundamental and optical band gaps. The Sb_2O_3 material has an optical band gap in a suitable range as a transparent conducting oxide, and the sulphide and selenide materials have suitable band gaps for thin film solar cell absorbers.

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Figure 14: A schematic illustrating the interaction between the Sb^{III} cations and chalcogenide anions and the change in their respective energy levels down the series.

7. References

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