1. Introduction

Transparent conducting oxides (TCO) are important materials in the development of energy-related devices such as solar cells and light emitting diodes. One of the major issues with these TCOs is the lack of effective p-type TCO materials, which prevents the creation of transparent electronic devices [1, 2]. Traditional TCO materials such as In$_2$O$_3$ and SnO$_2$ can be readily doped n-type, but have yet to be successfully doped p-type [3]. This large doping asymmetry originates from a common electronic structure feature of these TCO materials, namely that their highest energy valence states consist mainly of O-p and their lowest conduction states consist mainly of the cation s. Therefore, these materials possess large ionization energies and high electron affinities, making them strongly resistive to p-type doping.

In order to improve the p-type doping propensity, the nature of the filled valence bands has to be changed. One approach is to introduce filled M-d levels, which are usually higher in energy than the O-p level. For example, this occurs in Cu$_2$O, which is p-type due to intrinsic defects that produce hole states. However, while these holes are relatively mobile, the Cu$_2$O band gap of 2.1 eV [4] is too low for a TCO. Copper based delafossites, such as CuAlO$_2$ [5], have larger band gaps due to the 2D nature of their crystal structure. However, their application as TCOs is impaired by their low hole mobility, which is also a result of this layered structure [6, 7]. This mobility drawback makes another approach attractive: replacing O with another chalcogen element such as S or Se. While this could result in more disperse bands, it is possible that this would also come at the price of a smaller band gap. The p states of these elements are usually higher, making their compounds more prone to being p-type doped. In past years, there has been some effort to investigate the potential of using Cu-containing chalcogenides, such as LaO$_x$CuS [8]...
and BaCu$_2$S$_2$ [9], as p-type transparent semiconductors. The possibility of increased hole mobility in these chalcogenides, compared to their oxide counterparts, is also a promising one.

The electronic structures of these chalcogenide compounds have not been thoroughly studied by first principles methods. BaCu$_2$S$_2$ was recently examined using semi-local functionals and found to have a calculated band gap of 0.50 eV [10]. However, these functionals typically underestimate the band gap and are not well-suited to assess a material’s potential as a transparent semiconductor. The experimental measurement of 1.75 eV for BaCu$_2$S$_2$ may also be larger than its actual gap because of the exceedingly low density of states (DOS) at the conduction band edge and the small optical oscillator strength [9]. While semi-local functionals generally underestimate the band gap, hybrid functionals have been shown to give a more accurate band gap in comparison with experimental values [13].

The doping propensities of these chalcogenide compounds have also not been thoroughly studied. However, the band alignments of semiconductor materials may provide guidelines in understanding their doping propensities, as these band alignments relate directly to their ionization energies and electron affinities. Generally, materials with smaller ionization energy are prone to p-type doping, whereas materials with larger electron affinity are prone to n-type doping.

In this contribution, the electronic structures of Ba$_M$$_2$X$_2$ ($M = Cu, Ag; X = S, Se$) compounds have been calculated using the density functional theory (DFT) method with both semi-local and hybrid functionals. The bands of these compounds are aligned with the vacuum level by calculating the electrostatic potential profile of a slab and vacuum supercell. The results show that the compounds have small ionization energies, indicating a potential ability to be p-type doped, but that their electronic band gaps are smaller than desired for TCOs. The substitution of Ag for Cu opens the band gaps slightly while retaining nearly the same ionization energy.

2. Computational methods

The electronic structure calculations and geometry optimizations are based on the DFT method as implemented in the Vienna Ab-initio Simulation Project (VASP) code [11]. The projector augmented wave (PAW) potentials are used to describe the ionic potentials of the elements. In order to examine the effect of the different choice of functional, both semi-local Perdew–Burke–Ernzerhof (PBE) generalized gradient approximated (GGA) functionals and the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional were employed [12, 13]. While the PBE functional was sufficient enough to obtain lattice parameters, DOS, and band structure, it tends to underestimate the band gap. The HSE hybrid functional was chosen because it is one of the hybrid functionals that is available in a solid state code such as VASP. It also includes a screening of the exchange functional that has been demonstrated to work for most semiconductor materials. An $8 \times 8 \times 4$ Monkhorst–Pack $k$-mesh was used for all of the PBE calculations, whereas a $6 \times 6 \times 2$ $k$-mesh was used for HSE calculations. Due to the high computational load of the HSE calculations, a reduced $k$-mesh was used to give a greater probability of convergence.

A cutoff energy of 550 eV was found to be sufficient to obtain accurate forces and stresses for the geometry optimizations because the recommended ENMAX for the PAW potentials for Ba, Cu, Ag, S, and Se were all significantly lower than this.

Slab model calculations were performed to find the alignment of the valence band maximum (VBM) and conduction band minimum (CBM) relative to the vacuum level [14, 15]. A supercell was constructed and stacked along a non-polar direction to minimize the problem of surface dipoles (b as shown in figure 2), using the optimized atomic structure obtained by the PBE functional. The supercell consisted of a bulk region of six...
unit cells and a vacuum region of the same length. The slab was chosen to be thick enough so that the center would represent the bulk material and reliably align the band edge states of the different materials. The electrostatic potential of the bulk region was then aligned with the vacuum region center to determine the alignment of the VBM and CBM relative to the vacuum. The ionization energy $E_I$ and the electron affinity $E_A$ are calculated by:

$$E_I = \Phi_{el} - E_{VBM}$$

$$E_A = \Phi_{el} - E_{CBM}$$

(1)

in which $E_{VBM}$ and $E_{CBM}$ are the absolute values of the VBM and CBM energies obtained from bulk calculations, and $\Phi_{el}$ is the electrostatic potential difference between the bulk center and the vacuum as calculated from the slab model. This electrostatic potential difference was extracted from the LOCPOT file using the program macroave.

3. Results and discussion

The chalcogenide Ba$_M$X$_2$ compounds are composed of divalent cations (Ba$^{2+}$), monovalent transition metal cations (Cu$^+$ or Ag$^+$), and divalent anions (S$^{2-}$ or Se$^{2-}$). They crystallize in the ThCr$_2$Si$_2$ structure type ($I4/mmm$ space group), consisting of layers of edge-sharing MX$_4$ tetrahedra, separated by Ba$^{2+}$ cations. The Ag compounds have not been synthesized experimentally, but are investigated here theoretically. BaAg$_2$S$_2$ is known to form in the La$_2$O$_3$ structure type \[16\], and our total energy calculations find that it is more stable in this structure than in the hypothetical ThCr$_2$Si$_2$ structure by 0.17 eV/cell. However, it may still be a worthwhile endeavor to investigate this potentially metastable form of BaAg$_2$S$_2$ based on comparisons of its calculated energy of reaction to that of BaCu$_2$S$_2$, which are $-4.17$ eV and $-4.56$ eV, respectively. Table 1 lists the experimental and calculated values of the lattice constants, the $z$ position of $X$, and the $M$–$X$ bond lengths. The PBE and HSE geometry parameters are both in good agreement with the experimental values. The replacements of both Cu and S with larger ions lead to increasing lattice parameters as well as increasing $M$–$X$ distances. The replacement of Cu by Ag has a more significant effect than of S by Se, which is consistent with a larger radii difference for Cu$^+$ (0.60 Å) and Ag$^+$ (1.00 Å) ions than for S$^{2-}$ (1.84 Å) and Se$^{2-}$ (1.98 Å) ions \[17\].

The calculated electronic band structures of the four compounds are shown in figure 3 using both the PBE and HSE functionals, with PBE covering the full Brillouin zone and HSE only the $Y$ to $\Gamma$ to $M$ dispersion. The highest valence band and lowest conduction band from the HSE hybrid functional are overlaid in bold orange lines to illustrate its larger bandgap. The direct band gap occurs at the $\Gamma$ point.

![Figure 3. Electronic band structures of Ba$_M$X$_2$ ($M$ = Cu, Ag; $X$ = S, Se) as determined by PBE calculations along the $Y$ to $\Gamma$ to $M$ dispersion. The highest valence band and lowest conduction band from the HSE hybrid functional are overlaid in bold orange lines to illustrate its larger bandgap. The direct band gap occurs at the $\Gamma$ point.](image)

| $a = b$ (Å) | $c/\sqrt{3}$ | $z$ | $M$–$X$ (Å) |
|-------------|-------------|-----|-------------|
| BaCu$_2$S$_2$ | 3.92 | 3.94 | 3.91 \[18\] | 3.23 | 3.23 | 3.24 \[18\] | 0.361 | 0.361 | 0.362 \[18\] | 2.41 | 2.42 | 2.41 \[18\] |
| BaAg$_2$S$_2$ | 4.14 | 4.12 | — | 3.29 | 3.33 | — | 0.378 | 0.377 | — | 2.70 | 2.70 | — |
| BaCu$_2$Se$_2$ | 4.06 | 4.09 | 4.04 \[18\] | 3.23 | 3.24 | 3.26 \[18\] | 0.363 | 0.364 | 0.361 \[18\] | 2.52 | 2.54 | 2.50 \[18\] |
| BaAg$_2$Se$_2$ | 4.26 | 4.24 | — | 3.33 | 3.36 | — | 0.378 | 0.377 | — | 2.80 | 2.79 | — |

Table 1. The calculated and experimental lattice constants ($a = b$), $c/\sqrt{3}$ ratio, $z$ position of $X$, and $M$–$X$ bond lengths for Ba$_M$X$_2$ ($M$ = Cu, Ag; $X$ = S, Se) compounds.
Table 2. The calculated and experimental band gaps for the BaM$_2$X$_2$ compounds. The band gap for strontium substituted compounds are also included to show that there are possible substitutions that can increase the band gap.

| Material         | PBE   | HSE  | EXP |
|------------------|-------|------|-----|
| BaCu$_2$S$_2$    | 0.51  | 1.62 | 1.75 [9] |
| BaAg$_2$S$_2$    | 0.91  | 2.01 | —   |
| BaCu$_2$Se$_2$   | 0.36  | 1.33 | —   |
| BaAg$_2$Se$_2$   | 0.68  | 1.61 | —   |
| SrCu$_2$S$_2$    | 0.51  | 2.27 | —   |
| SrCu$_2$Se$_2$   | 0.26  | 2.03 | —   |

valence bands and the upward shift of the conduction bands are similar; whereas the shift of the conduction bands is more significant for Ag compounds. Replacing S with Se reduces the band gap by about 0.3 eV and seems to make the bands more dispersive; whereas replacing Cu with Ag increases the gap by about 0.4 eV. For further comparison, the band gaps of SrCu$_2$S$_2$ and SrCu$_2$Se$_2$ were also calculated. In the Ag compounds, the replacement of Ba with Sr increases the band gap by about 0.3 eV, showing that similar substitutions may further increase the band gap to a more ideal value.

The band gap of BaCu$_2$S$_2$ was experimentally determined to be 1.75 eV [9]. The HSE result of 1.62 eV matches well with this experimental value, and the slight discrepancy is likely caused by the low DOS close to the CBM. The band gaps of the other compounds are not known experimentally. The conduction bands of the four compounds are largely dispersed around the Γ point and are low in energy compared to conduction states in the other areas of the Brillouin zone, resulting in a very low DOS close to the CBM. This feature also occurs in many nitride and oxide semiconductors, such as InN and ZnO. For example, the gap of InN was originally measured to be 2.0 eV for films deposited by sputtering and MOVPE, [19, 20]; however, further investigation of MBE films established the true gap of InN as 0.7 to 0.8 eV [21]. The small band gaps of some of these compounds suggest that they are not ideal candidates for p-type transparent conducting behavior.

In order to investigate the nature of the electronic states around the VBM and CBM, the wavefunctions were projected into the atomic orbitals inside the PAW radii for each element. As shown in figure 4, the valence states consist of mainly the transition metal (Cu or Ag) d orbitals and the chalcogen (S or Se) p orbitals. The partial DOS (PDOS) of the sulfides and selenides with the same cations are quite similar except that in the selenides, the gaps are slightly smaller and the bands are slightly broader. On the other hand, the PDOS shows very different features for the Cu and Ag compounds. In BaCu$_2$S$_2$ and BaCu$_2$Se$_2$, the states close to the VBM are dominantly Cu-d states. The S-p and Se-p orbitals are lower in energy, at about 3 to 6 eV below the Fermi level. In contrast, the states close to the VBM of BaAg$_2$S$_2$ and BaAg$_2$Se$_2$ consist of both Ag-d and S-p (Se-p) orbitals. The peak of the Ag-d states are 3 to 5 eV below the Fermi level. The hybridization of the d and p orbitals reduces the localization of hole states around the VBM and thereby increases the hole mobility [10]. The states close to the CBM are composed of, to some extent unexpectedly, mainly Ba-d. In the Ba atom, the s state is filled before d in accordance with the Aufbau principle. However, the Ba-s orbital has a very large radius. Upon forming the extended solid, the narrow space may push up the energy of these orbitals and become higher than that of the d orbitals.

A recent DFT study of the BaS electronic structure also shows that the Ba-d orbitals are the dominant components of the states around the CBM [22]. Slab model calculations were conducted to achieve absolute energy alignment by aligning the average electrostatic potential of the bulk materials with that of the vacuum level. For these compounds, it was necessary to construct the slab model along a non-polar orientation to avoid a large polarization that can originate from the surface discontinuity. The calculated electrostatic potential profiles are shown in figure 5. The relaxation of the atoms in the c direction, perpendicular to the slab, may cause noticeable surface dipoles, causing the dips and bumps in the potential profile around the surface regions. For most of the compounds, the effect is small enough that it does not cause significant change in the potential alignment. However, the atomic relaxation at the surface is quite large for BaAg$_2$S$_2$ (red line in figure 5), causing a non-negligible change in the alignment. The band alignment difference with relaxation and non-relaxation along the perpendicular direction is as large as 0.8 eV.

The alignments of the VBM and the CBM to the vacuum level are shown in figure 6, and the corresponding IE and EA values are presented in table 3. In contrast with oxides and nitrides, for which the p-type doping processes are impeded by exceedingly large IEs, the IE and EA values are quite small for these four sulfide and selenide compounds. Their IE values vary over a small energy range from 4.5 to 5 eV. GaN has an IE value of about 6.5 eV, and is well known for its difficulty to dope p-type [23]. The success in overcoming this issue by doping Mg in GaN was the major step toward the fabrication of blue and UV nitride LED and laser diodes [24]. The IE is even higher for ZnO (about 8 eV) [25], and its p-type doping is still the major challenge for its application as an optoelectronic material. On the other hand, it may be difficult to n-type dope the BaM$_2$X$_2$ materials of this study because their EA values are very low. Indeed, since the states around the CBM consist mainly of Ba-d states, one needs to transfer the electrons from donor states into these Ba-d states in order to make n-type doping possible.

The band alignments are quite similar for the four compounds. While the VBM position among the compounds varies over 0.5 eV, the CBM position is nearly constant. The VBM position of the Ag compounds is lower than that of the Cu compounds because of the difference in energy of their d levels. However, upon comparing the PDOS of the compounds with the different transition metals (figure 4), the Cu-d states dominate the edge of the VBM, whereas the Ag-d states are several eV lower than the VBM. This same difference between Cu and Ag occurs in the related layered delafossite oxides [26].

4. Conclusion

The DFT method, using both semi-local and hybrid functionals, was used to calculate the electronic structures
and band alignments of BaCu$_2$S$_2$ and BaCu$_2$Se$_2$, and the theoretical compounds of BaAg$_2$S$_2$ and BaAg$_2$Se$_2$, including their ionization energies and electron affinities. The band gaps from the hybrid calculations are between 1.33 and 2.01 eV, a bit too small for ideal transparent conducting behavior. However, the low ionization energies and the small electron affinities of these compounds suggest a strong propensity to be p-type doped. While the replacement of S by Se decreases the band gap, the replacement of Cu by Ag significantly increases the band gap and maintains the small ionization energy, therefore retaining the tendency toward p-type doping. The problem of a low band gap is also not impossible to address because other substitutions, such as replacing Ba with Sr, provide ways to increase it. Therefore, though the band gap of these compounds may not be ideal, in future transparent conducting materials, it may be a viable option to consider the possibility of replacing O with S and Se to increase conductivity and hole mobility as well as to replace Cu with Ag to increase the band gap.

Table 3. The calculated ionization energies and electron affinities for the BaM$_2$X$_2$ compounds. Experimental values are unavailable.

| Compound     | $E_I$ (eV) | $E_A$ (eV) |
|--------------|------------|------------|
|              | PBE        | HSE        | PBE        | HSE        |
| BaCu$_2$S$_2$ | 3.78       | 4.76       | 3.27       | 3.14       |
| BaAg$_2$S$_2$ | 4.71       | 5.39       | 3.80       | 3.37       |
| BaCu$_2$Se$_2$| 3.67       | 4.50       | 3.31       | 3.17       |
| BaAg$_2$Se$_2$| 4.43       | 4.99       | 3.75       | 3.38       |

Figure 4. Electronic densities of states for BaM$_2$X$_2$ ($M$ = Cu, Ag; $X$ = S, Se) as determined by PBE calculations. The projected DOS are displayed for the atomic orbitals contributing near the band edges.

Figure 5. The calculated electrostatic potential profiles for BaM$_2$X$_2$ ($M$ = Cu, Ag; $X$ = S, Se) as determined by slab PBE calculations. The solid and dashed lines respectively present the results obtained by fully relaxing the atomic positions and by fixing them perpendicular to the slab, along the $c$ direction.

Figure 6. Electronic band offset diagram for BaM$_2$X$_2$ ($M$ = Cu, Ag; $X$ = S, Se) as determined by slab PBE calculations. The band gaps are taken from bulk HSE calculations.
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