

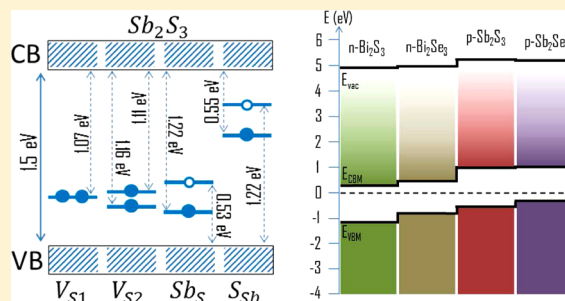
Unraveling the Native Conduction of Trichalcogenides and Its Ideal Band Alignment for New Photovoltaic Interfaces

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ABSTRACT: The trichalcogenides Sb_2S_3 , Sb_2Se_3 , Bi_2S_3 , and Bi_2Se_3 share an orthorhombic crystal structure and have recently been pointed out as promising materials for application in solar energy harvesting, such as photovoltaic solar cells, because of their ultimate structural and electronic/optical properties. In this work, using a first-principles theoretical approach, we investigated the origin of the electrical conduction in bulk systems as well as the energy band alignment in different heterostructures composed of these compounds. In the first part, formation energy and thermodynamic transition energy of native point defects are evaluated. In the second part, surface properties such as free energy and electron affinity were obtained. In the third part, the energy alignments of some possible heterostructures were proposed. The excellent agreement between theoretical results and reported experimental values indicates that these trichalcogenides have their electrical properties ruled by native point defects, mainly antisites. The energy alignment between the trichalcogenides and usual photovoltaic substrates shows that these materials can be successfully applied to the construction of type-II staggered heterojunctions. A last analysis is done by considering only homo- and heterojunction of trichalcogenides, showing that these materials could lead to high-efficiency cells with broad spectral absorption and high conduction/valence band offsets.



INTRODUCTION

The search for renewable energy sources rather than being an ecological issue has become a real necessity because of emptying of the usual fossil resources as energy demand only increases. In this context, the solar-light-based technologies overcome other types of renewable sources such hydro and wind power by being less sensitive to climate events. The state-of-art solar cells based on photovoltaic effects reach energy conversion efficiencies up to 45% in academic prototypes of multijunctions,^{1,2} where three or more semiconductors junctions are hold together to optimize the absorption in different ranges of the solar spectrum, attaining high gains and breaking the Shockley–Queisser limit for single junctions. Nonetheless, the usual commercial cells based on single silicon junctions or thin films can reach a maximum efficiency of 15% and are much cheaper than multijunctions architectures but are still expensive when compared to fossil or nuclear energy sources.

Nowadays, rather than a frenetic search for a few percent increase in cell efficiency, important achievements are related to relevant reduction in production and implementation costs. The development of less-expensive solar cells strongly depends on the discovery of new materials and processes, good examples being the organic solar cells (OSC),³ dye-sensitized solar cells (DSSC),^{4,5} quantum dots based solar cells (QDSC)^{6,7} and chalcogenides thin films based solar cells.⁸ However, further developments are still needed in these areas for future applications.

Solar cells based on thin films play an important role in solar energy conversion, mainly by being cheaper and easier to fabricate and presenting similar efficiency when compared to cells based on single crystals. Related to this, chalcogenides compounds such as CdTe , CuInSe_2 (CIS), CuGaSe_2 (CGS), and $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGS) show solar cell ultimate properties such as high optical absorption in the solar spectrum, direct band gap that can be tuned in between 1.0 and 1.7 eV, and unpinned Fermi level leading to high open-circuit voltages (OCVs).² Together, CdTe and CIGS are about 10% of the market of solar cells and have reached efficiencies up to 20%. In the past few years, new groups of chalcogenides have appeared as excellent candidates for light-to-electrical energy conversion, such as the dichalcogenides^{9,10} and the trichalcogenides.^{11,12}

Among the trichalcogenides materials, the four compounds Sb_2S_3 , Sb_2Se_3 , Bi_2S_3 , and Bi_2Se_3 are attracting attention because of excellent absorption of the solar spectrum and their response in quantum dot based cells,^{11,13–15} inorganic sensitizers,^{16–18} and low-cost single junctions.¹⁹ These four compounds share the same orthorhombic crystal structure (space group $Pnma$) and a band gap in the range of 1.2–1.7 eV,^{20–23} with Sb_2S_3 and Bi_2Se_3 having a direct band gap and the other two being indirect. Some remarkable properties as well as the potential for

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solar energy harvesting have been demonstrated in early reports, such as the existence of a benign grain boundary that occurs because of small van der Waals coupling between layers leading to 1D anisotropic orthorhombic structure¹³ and the possibility of the formation of a defect-free interface with other compounds reducing the recombination centers.²⁴ Excellent electrical properties, such as electrical resistivity, are demonstrated for Sb₂Se₃²⁵ that could lead to higher power conversion and less voltage losses.

Nanocrystals of Sb₂S₃ and Bi₂S₃ have been successfully used as sensitizer in nanoheterojunctions and solution-processed solar cells^{11,15,18,26} and in photodetectors,²⁷ leading to efficiencies of about 5%. Reports on thin films based cells of X₂Y₃ (for X = Bi and Sb and Y = S and Se) compounds showed energy conversions up to 5%.^{13,16,28,29} For the case of Bi₂Se₃ with orthorhombic crystalline structure, no experimental data was found to support the use of this compound in solar cell, but theoretical works have indicated that interesting results should be expected.³⁰ In summary, the potential application of this group of materials is considerably high; however, some fundamental obstacles such as the lack of information on electronic, electrical, and optical properties still limit the improvement of the devices.

The current research challenges on the X₂Y₃ compounds based solar cells are related to the enhancement of efficiency to values closer to commercial ones, i.e., up to 15%, that strongly rely on the control and improvement of electrical properties of these materials. However, it is well-determined that electrical parameters such resistivity, carrier density, carrier type, and carrier activation energy depend on the synthesis process and parameters. The origin of the carriers and the conduction mechanism in X₂Y₃ compounds as well as the cause of the large dispersion in the measured electrical parameters remain as open questions. For Sb₂S₃, intrinsic p- and n-type behaviors was determined experimentally,^{31,32} and electrical resistivities between 10⁴ and 10¹⁰ Ω·cm were observed.^{31,33} For Bi₂S₃, just the n-type character has been reported with electrical resistivity ranging from 0.05 to 10⁶ Ω·cm.^{34,35} In the case of Sb₂Se₃, resistivity of about 10⁵ Ω·cm²² and p-type character were found,³⁶ whereas for nanostructures, much lower values of about 3.10⁻² Ω·cm and n-type conduction were described.²⁵ Bi₂Se₃ also presents n-type conduction with resistivity of about 10⁴ Ω·cm, as measured by our group (unpublished work). For the sake of a future solar technology grown on the basis of trichalcogenides, control and optimization of the electrical and optical properties of these compounds is a fundamental step that depends on the understanding of the conduction mechanism as well as the origin of the electronic carriers.

Here we report a theoretical study of the native point defects and their impact on the electrical properties and energy band alignment of the compounds X₂Y₃ (X = Sb and Bi; Y = S and Se). For this purpose, ab initio calculations based on the density functional method were used to obtain the formation and transition energies of several point defects. Our results show that the most stable defects deeply depend on the growth conditions and effectively explain the conduction type as well as the activation energies found experimentally. Once knowing the energy alignment for these compounds, we propose different scenarios of semiconducting hetero- and homojunctions that may lead to a high efficiency of solar energy conversion.

THEORETICAL METHODS

Method. The density functional theory (DFT)-based³⁷ calculations were done with the VASP package,³⁸ which employs a plane wave basis set and periodic boundary conduction to simulate bulk crystals. A gradient-corrected xc functional (GGA) was used in the parametrization of revised Perdew–Burke–Ernzerhof (PBEsol) functional,³⁹ and the valence electrons were described by the pseudopotential approximation being the core–valence interaction treated by PAW method.⁴⁰ To simulate a well-behaved dilution of defects, a supercell approach was used containing 60 atoms that were relaxed in a fully spin-polarized scheme without spin–orbit coupling (SOC). After relaxation, the total energy was calculated including SOC. The lattice parameters *a*, *b*, and *c* used in this work are 11.281, 3.828, and 10.908 Å for Sb₂S₃, 11.783, 3.978, and 11.311 Å for Sb₂Se₃, 11.162, 3.963, and 10.942 Å for Bi₂S₃, and 11.711, 4.102, and 11.404 Å for Bi₂Se₃, being obtained by optimization using PBEsol that leads to structural parameters closer to experimental values than other functionals.³⁰

Computational Details. The plane wave expansion cutoff energy was 240 eV for all compounds, and the k-sampling for the reciprocal space integrations was a mesh with size 4 × 4 × 4, which leads to at least 27 irreducible points in the first Brillouin zone (BZ). For SOC calculations, the mesh was reduced to 3 × 3 × 3, with the same minimum of 27 irreducible points in BZ. The convergence criterion to self-consistency was set to 10⁻⁶ eV, and the force threshold for relaxation was 0.01 eV/Å.

Defect Energies. The formation energies of the defects were calculated with the following expression,

$$\Delta H_f(D, q) = E(D, q) - E^H + \sum_i N_i(E_i + \mu_i) + qE_F \quad (1)$$

where $E(D, q)$ is the total energy of a supercell containing a defect *D* and in a charged state *q*, E^H is the total energy of a host supercell (no defects and no charge), N_i is the number of *i* atoms added or removed from the cell, E_i is the reference energy of the atom *i*, i.e., the chemical potential of the pure element calculated in solid form, and μ_i is the chemical potential of the reservoir of atoms, as described below. E_F is the Fermi energy calculated by $E_F = \varepsilon_{\text{VBM}} + \Delta E_F$, where ε_{VBM} is the aligned valence band maximum for the defective supercell (calculated by quasi-particle, $\varepsilon_{\text{VBM}} = E_{q=+1}^H - E^H$) and ΔE_F is the relative Fermi level inside of band gap.

The calculation of the thermodynamic transition energies, i.e. energies needed to charge or discharge a defect level, was done on the basis of a quasi-particle approach, in which an extra charge is added to the supercell, occupying the next available electronic level, and obtained by the formula below,

$$\varepsilon_D(q/q') = \frac{\Delta H_f(D, q) - \Delta H_f(D, q')}{q' - q} \quad (2)$$

where q' is the charge after the transition, q is the charge before the transition, and *D* is the defect type. The transition energy can be directly compared to activation energy E^A by using the expression $E_D^A(q/q') = \varepsilon_{\text{CBM}} - \varepsilon_D(q/q')$ for donor levels and $E_D^A(q/q') = \varepsilon_D(q/q') - \varepsilon_{\text{VBM}}$ for acceptor levels.

Equilibrium Conditions. The conditions used for calculating μ_i were based on two distinct environments: one free of anions (cation-rich: S- or Se-rich) and the other free of

cations (anion-rich: Sb or Bi). To simulate this, the constraint $\Delta H_{X_2Y_3} \geq 2\mu_X + 3\mu_Y$ was taken, with $\mu_X = 0$ or $\mu_Y = 0$ for cation- or anion-rich, respectively. The enthalpy of formation of each compound ($\Delta H_{X_2Y_3}$) was calculated, and the obtained values are -3.19 , -1.36 , -5.45 , and -3.89 eV for the Sb_2S_3 , Sb_2Se_3 , Bi_2S_3 , and Bi_2Se_3 , respectively.

Corrections. To obtain formation energies as accurate as possible for the defects, some corrections need to be done because of the finite size of the supercell and the haziness of DFT in calculating band gaps. Three corrections were used: first, a potential alignment using core levels, second, a charge image correction due electrostatic interaction between periodic images of the supercell, and last, a conduction band edge correction. All the correction follows the formalism used by Lany and Zunger.^{41,42} The band gap of the trichalcogenides used for the band edge correction were 1.5 eV for Sb_2S_3 , 1.3 eV for Sb_2Se_3 , 1.4 eV for Bi_2S_3 , and 1.2 eV for Bi_2Se_3 .⁴³

Defects. Many types of point defects could be calculated, such as vacancies, antisites, and interstitials. Moreover, the orthorhombic crystal structure of these materials has three distinct symmetry sites for anions and two distinct sites for cations, increasing the amount of possible defects to be considered. In this work only the most stable defects, i.e., defects with lower formation energy, will be taken into account for the calculations. These defects are the S or Se and Sb or Bi antisites and two distinct types of anion (S or Se) vacancies.

Surfaces. For the estimation of the surface free energy and the electron affinity, slab calculation was performed by introducing a vacuum gap of 20 Å along the selected plane direction. The stoichiometric slab was composed of 60–120 atoms, depending on the surface, (100), (010), or (001). For the calculation of the electron affinity the following formula was used,

$$\chi_e = W_F - E_g + (E_F - E_{VBM}) \quad (3)$$

where $W_F = U_e^{\text{vacuum}}(\infty) - E_F$, $U_e^{\text{vacuum}}(\infty)$ is the electrostatic potential far from the surface and deep in the vacuum layer, E_g is the single-particle band gap from the slab calculation, and E_{VBM} is the energy of the valence band maximum. For the calculation of the surface free energy, we used

$$S_F = \frac{(E_t^{\text{slab}} - N_i E_i)}{2A} \quad (4)$$

where E_t^{slab} is the total energy of the slab calculation, N_i is the number of X_2Y_3 molecules in the slab, E_i is the energy of a bulk single molecule, and A is the surface area.

RESULTS AND DISCUSSIONS

Point Defects. The orthorhombic ($Pnma$) crystalline structure shared by the X_2Y_3 compounds is presented in Figure 1a. For simplicity, it will be presented the case of Bi_2S_3 , but the same description follows for the other compounds. The crystal is composed of 1D ribbons along $[010]$ direction (indicated by the dashed rectangle in Figure 1a) that are connected to other ribbons along $[001]$ direction by a weak Bi–S (X – Y in the generalized case) interaction, whereas along $[100]$ direction the ribbons stack forming a layered structure driven by weak van der Waals interaction. These 1D structures are responsible for the appearance of van Hove singularities (peaks in the density of states)⁴⁴ as well as the high dispersion of the valence band between Γ – Y high symmetry point in BZ that leads to a low

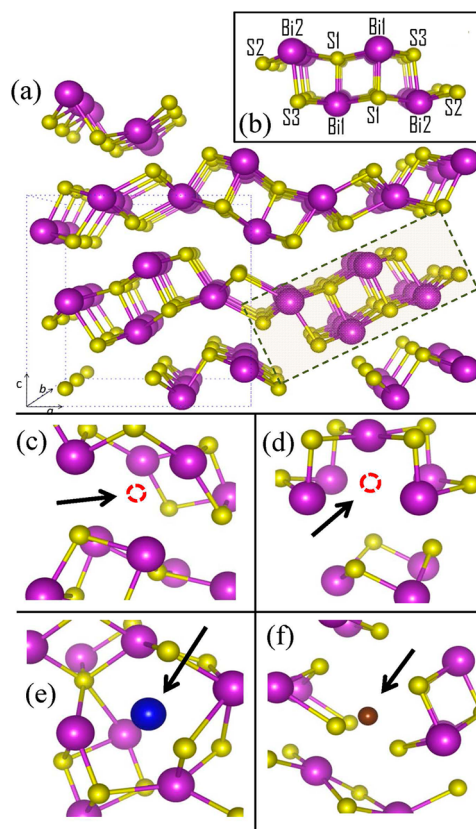


Figure 1. (a) Crystal structure of Bi_2S_3 (X_2Y_3) and (b) zoom over a single ribbon of $(Bi_2S_3)_2$, indicating the nonequivalent atoms in the structure. (c and d) Local environments of S1 (V_S^1) and S2 (V_S^2), vacancies, respectively, and (e and f) local environments of Bi (Bi_S^2) and S (S_{Bi}^2) antisites, respectively. The point defects are indicated by arrows.

effective mass, high conductivity, and anisotropic conduction in these solids.^{31,45,46} In Figure 1b, a single ribbon is presented showing the three and two nonequivalent sulfur and bismuth atoms, respectively. The sulfur occupying a site labeled S1 has five Bi nonequidistant near neighbors (NNB), whereas the sites S2 and S3 present a low coordination with three Bi NNB, mainly differing by the bond lengths and bond angles. The bismuth sites Bi1 and Bi2 show nonequidistant five and six coordination, respectively.

In Figure 1c–f are presented the local environments for vacancies S1 and S2, Bi atom in a S2 antisite (blue sphere indicating the antisite), and a S atom in a Bi2 antisite (brown sphere). For S3 vacancies (or Y3 vacancies in the general case of X_2Y_3), properties similar to those of S2 vacancies were found. Other defects such as Bi1 and S1 antisites presented too-high formation energies and would exist in very small concentrations in these compounds. The same happens to interstitial defects that in addition introduce large distortions in the supercell.

The formation energy of neutral defects calculated by eq 1 for two different thermodynamic growth conditions, cation- and anion-rich, are indicated in the graphs of Figure 2. In Figure 2a, for the compound Sb_2S_3 in a situation with a high abundance of S, a large concentration of S_{Sb}^2 antisites (sulfur in a place of a Sb2 atom) should be expected. Reducing the chemical potential of the S reservoir and increasing Sb in order to reach the Sb-rich condition, an intermediate situation

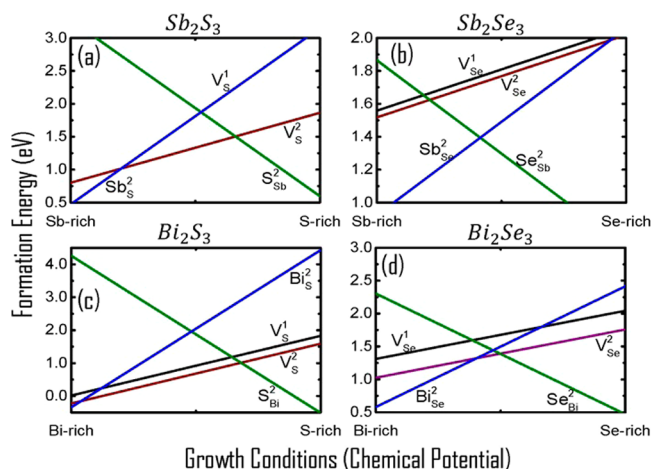


Figure 2. Formation energy depending on the synthesis condition for different kind of defects in the compounds (a) Sb_2S_3 , (b) Sb_2Se_3 , (c) Bi_2S_3 , and (d) Bi_2Se_3 .

dominated by sulfur S1 and S2 vacancies (V_S^2 and V_S^1) is observed followed by a region dominated by Sb_S^2 antisites (antimony in a place of a S2 atom). In the case of Sb_2Se_3 , shown in the Figure 2b, the antisite defect Se_{Sb}^2 (selenium in a place of a Sb2 atom) dominates at growth conditions rich in Se. By moving to a growth condition rich in Sb, the defects concentration is dominated by Sb_{Se}^2 antisites (antimony in a place of a Se2 atom). For this compound, the defects distribution is dominated by the antisites, i.e., changing the chemical potential of the reservoir will only invert the concentrations between Se2 and Sb2 antisite defects. Systems where antisites are predominant defects usually occur when the constituent atoms possess similar sizes.^{47,48} In the system Bi_2Te_3 , the inversion in antisite concentration as a function of growth conditions can lead to an inversion in the carrier type.⁴⁹

Bismuth-based trichalcogenides, such as Bi_2S_3 shown in Figure 2c, should present high concentration of sulfur antisites (S_{Bi}^2) under conditions rich in sulfur because of the low formation energy, whereas under intermediate growth conditions, V_S^2 and V_S^1 vacancies should rule over others defects. Close to the bismuth-richest condition, the formation energy of Bi_S^2 antisites is comparable to the formation energy of the vacancies. In Figure 2d, for Bi_2Se_3 , the Se_{Bi}^2 and Bi_{Se}^2 antisites dominate the system over almost all growth conditions other than a small interval where V_{Se}^2 vacancies appear with smaller formation energy. From the results in Figure 2, it can be seen that sulfur vacancies can easily exist independently on the Sb or Bi cation and that increasing the atomic number of the constituent from S to Se or from Sb to Bi increases the energy difference between vacancies at sites 1 and 2 which can be attributed to a weakening of the bond between the sites X2 and Y2 due to the enhanced 1D character of the ribbons.

The transition levels induced by the point defects were studied by charging the supercell, and the results are summarized in Figure 3 for cation- and anion-rich growing conditions. In Figure 3a,b for sulfur V_S^1 and V_S^2 vacancies in Sb_2S_3 , by increasing the Fermi level (approaching the conduction band) the charge state of these defects changes because of the existence of electronic levels deep in the band gap. For the case of V_S^1 , for E_F close to the valence band, the most stable charge state is the doubly positive-charged, indicating that the lowest energy configuration is attained by

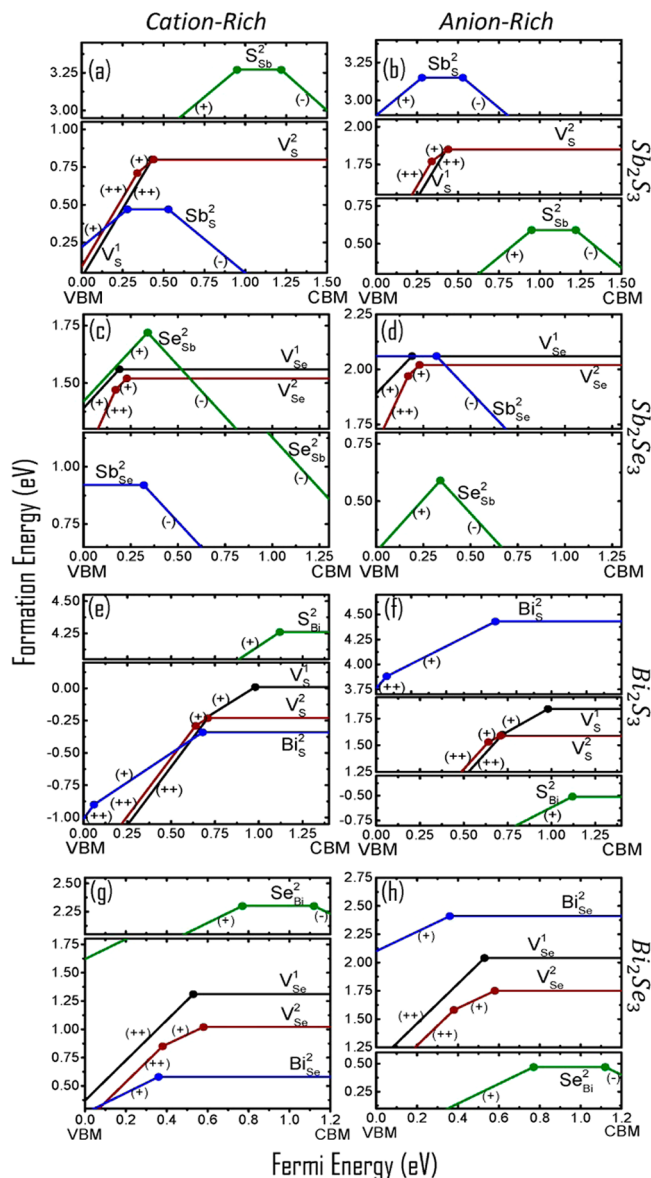


Figure 3. Formation energy of point defects for the Fermi level laying at different position inside of the band gap, for Sb_2S_3 (a and b), Sb_2Se_3 (c and d), Bi_2S_3 (e and f) and Bi_2Se_3 (g and h). The left column shows the cation-rich situation, i.e., Sb-rich and Bi-rich, and the right column shows anion-rich conditions, i.e., S- and Se-rich. VBM is the maximum of the valence band, and CBM is the minimum of the conduction band.

donating two electrons to the electron reservoir, i.e., the Fermi level. When the Fermi level is raised to $E_{V_S^1} (+2/0) = 0.43$ eV, the charge state of V_S^1 with smaller formation energy becomes neutral. The V_S^1 generates a single, doubly degenerated deep donor inside of the band gap of Sb_2S_3 , whereas the V_S^2 generates two deep donor levels at $E_{V_S^2} (+2/+) = 0.34$ eV and $E_{V_S^2} (+/0) = 0.43$ eV above VBM (valence band maximum). These type of defect-localized states (DLS) induced by the sulfur vacancies in the Sb_2S_3 usually pin the Fermi level on the middle of the band gap, leading to low carrier concentrations and high activation energies. For the antisite defects S_{Sb}^2 , two levels appear in the band gap: one donor at $E_{\text{S}_{\text{Sb}}^2} (+/0) = 0.95$ eV and one acceptor at $E_{\text{S}_{\text{Sb}}^2} (0/-) = 1.22$ eV, above VBM, which should contribute

to n-type conduction and reduce the resistivity in comparison to sulfur vacancies because these defects will help to keep E_F close to CBM (conduction band minimum). In the opposite situation, the antisite defects Sb_S^2 introduce two levels in the band gap: one donor at $\epsilon_{Sb_S^2} (+/0) = 0.28$ eV and one acceptor at $\epsilon_{Sb_S^2} (0/-) = 0.53$ eV, which are both above VBM and should dislocate E_F near the VBM inducing p-type conductivity. The presence of Sb_S^2 at high concentration may lead to an inversion of the carrier type in this compound, a situation that can be obtained by controlling the growth environment, as shown in Figures 2a and 3b.

The transition levels calculated for the selenium vacancies in Sb_2Se_3 show trends similar to those of Sb_2S_3 and are presented in Figure 3c,d. For cation-rich conditions, a single doubly degenerated deep level at $\epsilon_{V_{Se}^1} (+2/0) = 0.19$ eV for V_{Se}^1 and two donor levels at $\epsilon_{V_{Se}^2} (+2/+) = 0.17$ eV and $\epsilon_{V_{Se}^2} (+/0) = 0.23$ eV for V_{Se}^2 are obtained; however, the contribution of these defects should be less relevant because they present high formation energy. For the cation antisite Sb_{Se}^2 , a single acceptor level at $\epsilon_{Sb_{Se}^2} (0/-) = 0.32$ eV was found, whereas for the anion antisite Se_{Sb}^2 , a single, half-occupied doubly degenerated level appears at $\epsilon_{Se_{Sb}^2} (\pm) = 0.34$ eV. The main difference between the antisite defects in Sb_2S_3 and Sb_2Se_3 is that an extra positive charge added to the Sb_{Se}^2 supercell has higher formation energy than the Sb_S^2 whereas the addition of an extra electron to the Se_{Sb}^2 has much lower formation energy than in S_{Sb}^2 supercell that can be directly correlated to the slightly higher electronegativity of S in comparison to that of Se and Sb and strongly binds the electrons around itself. The results for Sb_2Se_3 would indicate a persistent p-type behavior and low electrical conductivities, on the basis of the existence of DLS close to the VBM that can easily be activated at room temperature independent of the growth conditions.

For the Bi_2S_3 compound, seven donor levels are found inside the band gap, as presented in Figure 3e: two at $\epsilon_{V_S^1} (+2/+) = 0.72$ eV and $\epsilon_{V_S^1} (+/0) = 0.98$ eV and another two at $\epsilon_{V_S^2} (+2/+) = 0.64$ eV and $\epsilon_{V_S^2} (+/0) = 0.71$ eV due to sulfur vacancies V_S^1 and V_S^2 , respectively. The other three are antisite defects with levels at $\epsilon_{Bi_S^2} (+2/+) = 0.06$ eV and $\epsilon_{Bi_S^2} (+/0) = 0.68$ eV in Bi_S^2 and a single level at $\epsilon_{S_{Bi}^2} (+2/0) = 1.12$ eV for S_{Bi}^2 . The absence of an acceptor level in Figure 3e,f suggests that only n-type behavior can be intrinsically found for this compound. The last case is Bi_2Se_3 shown in Figure 3g,h. The selenium vacancy V_{Se}^1 induces a single donor DLS at $\epsilon_{V_{Se}^1} (+2/0) = 0.53$ eV, the V_{Se}^2 induce one donor level at $\epsilon_{V_{Se}^2} (+2/+) = 0.38$ eV, and another one at $\epsilon_{V_{Se}^2} (+/0) = 0.58$ eV. Bi_{Se}^2 generates a single donor at $\epsilon_{Bi_{Se}^2} (+/0) = 0.36$ eV, and Se_{Bi}^2 generates one donor level at $\epsilon_{Se_{Bi}^2} (+/0) = 0.77$ eV and one acceptor at $\epsilon_{Se_{Bi}^2} (0/-) = 1.12$ eV. Again, only donor levels are found, suggesting persistent intrinsic n-type conduction for this compound.

Once knowing the transition energy of the defects, we can proceed to the discussion of activation energies and comparison with experimental data. In Figure 4 are shown four diagrams containing the thermodynamic activation energy for each X_2Y_3 compound. For Sb_2S_3 , this was experimentally determined for n-type samples under excess of sulfur an activation energy of 0.60 eV.⁵⁰ This value is in excellent agreement with the donor DLS reported here at 0.55 eV below CBM for the sulfur

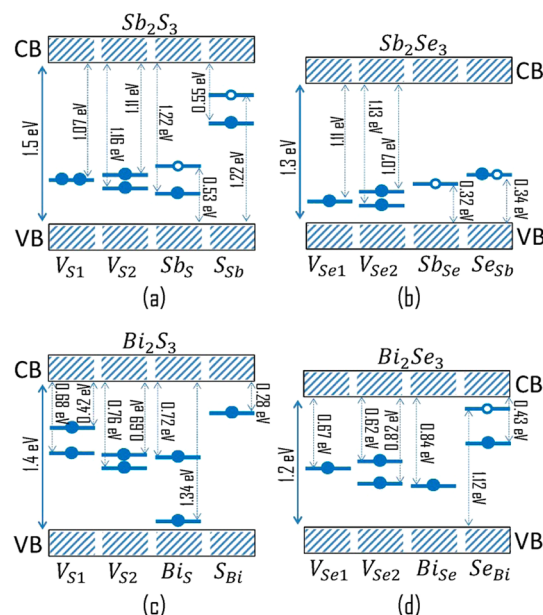


Figure 4. Band scheme of the X_2Y_3 compounds with the SPL laying inside of the band gap for (a) Sb_2S_3 , (b) Sb_2Se_3 , (c) Bi_2S_3 , and (d) Bi_2Se_3 . The closed circles indicate donor levels, whereas open circles stand for acceptors levels.

antisite. For p-type Sb_2S_3 , two activation energy were reported, 0.40 and 0.22 eV,³¹ which can respectively be directly correlated to an acceptor level at about 0.53 eV and to a donor level at 0.28 eV (both above VBM and induced by the antimony antisites, the last acting as a hole). The DLS at 0.53 eV was also confirmed by deep-level transient spectroscopy (DLTS) measurements⁵¹ and UPS.⁵² However, activation energies of about 1.1 eV were also reported for Sb_2S_3 that could be well-assigned to sulfur vacancies.⁵³ For Sb_2Se_3 , the reported values for activation energies for p-type samples lay between 0.50 and 0.65 eV²² that are little higher than those expected for antimony antisites and presented in Figure 4b; however, the existing experimental data is still insufficient for confirming the origin of the conductivity in this compound.

For bismuth-based sulfide, a persistent n-type behavior has been reported^{34,35,46} that is in complete agreement with the results obtained here because only donor levels are generated by the point defects. The measured activation energies reported for samples containing stoichiometric deviation to sulfur at about 0.28 eV³⁵ and 0.40 eV^{35,46} could be attributed to S_{Bi}^2 antisites as calculated in Figure 4c. Other reports⁵⁴ found higher activation energies, such 0.87 eV, which could be correlated to sulfur vacancies presenting DLS values between 0.69 and 0.76 eV. For the last compound, Bi_2Se_3 , the lack of information in the literature difficult the comparison to experiments. Reported values found for the activation energies of about 0.37 and 0.12 eV⁵⁵ and 0.32 and 0.09 eV in our own measurements (unpublished) and containing deviations to a higher selenium concentration and n-type behavior could be respectively connected to Se_{Bi}^2 defects that generate one single donor at 0.43 eV and an electron-trap at 0.08 eV, both below CBM, as shown in Figure 4d. In general, the comparison with experimental results previously reported has shown an excellent agreement with the DLS calculated in this work and explains properly the origin of the carriers in these compounds.

Electronics of the Interfaces. Once knowing the position of the DLS, we can estimate the position of the Fermi level

inside of the band gap of these materials.^{56,57} For the energy alignment at the interface of these materials the calculation of the electron affinity is required, so we proceed as follows. The electron affinity is found following the procedure described in the **Theoretical Methods** section, using the work function obtained in the calculation with an infinite 2D slabs split by a vacuum region. Figure 5 shows the results for surfaces (100), (010), and (001) slab calculation; only the three low-index surfaces were considered for this study.

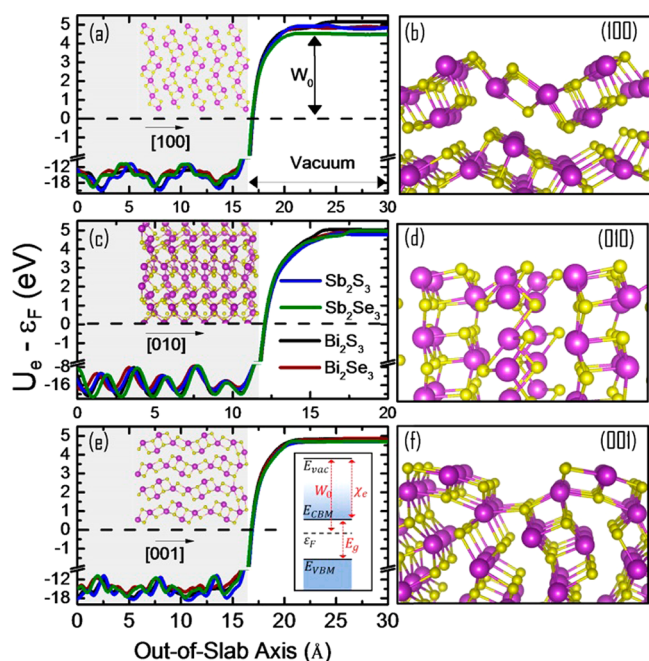


Figure 5. Electrostatic potential of the trichalcogenide compounds at the interface between the slab and vacuum, for surfaces (a) (100), (c) (010) and (e) (001), the line colors are specified in c. The atomic structures in b, d, and f represent the surfaces (100), (010), and (001), respectively, of the Bi_2S_3 compound. The inset in e shows the band scheme used for the calculation of the electron affinity (χ_e), where W_0 is the work function and E_g is the band gap.

In Figure 5a is presented the bidimensional averaged full electrostatic potential (electrostatic and XC potential) along the direction perpendicular to the plane (100) subtracted by the Fermi energy of the slab. Up to 17 Å in the x axis, the oscillations in potential indicate the presence of ions, and for higher x values, the potential goes to positive values until saturation, indicating the vacuum level. The saturation energy in the graph is the work function along the (100) surface for each of the X_2Y_3 compounds, and the calculated values are presented in the Table 1. Figure 5b shows the atomic structure for (100) slabs after the full relaxation of Bi_2S_3 , where the van der Waals separated surfaces are seen. Because of the more

closed structure of the 2D layers with no broken covalent bonds, the surface does not present structural distortions or reconstruction. The strong stability of this surface is reflected in the free surface energy, presented in Table 1, that shows a value of 5.97 meV/Å² for Sb_2S_3 which is much smaller than usual semiconductors such silicon of about 50 meV/Å².⁵⁸ For the other X_2Y_3 compounds, the surface free energy of the (100) surfaces shown in Table 1 slightly increase but are still relatively small. Such types of high stable surfaces can be well-applied to the construction of photovoltaic devices leading to a very low number of recombination centers.¹³ Figure 5c shows the averaged potential along [010] direction, indicating that the work function of X_2Y_3 compounds has similar values for this surface. In Figure 5d, the relaxed atomic structure of the surface (010) of the Bi_2S_3 is presented, where much higher distortion is found. The surface free energy for X_2Y_3 compounds is presented in Table 1, and values of about 20 meV/Å² were calculated. These higher values compared to (100) surfaces occur because of the existence of uncompensated bonds. In Figure 5e are presented the averaged potentials for all compounds along [001] direction, and Figure 5f shows the atomic structure of the (001) surface of Bi_2S_3 . A strong reconstruction of the surface can be seen, reducing the number of dangling bonds and decreasing the surface energy of the compounds in relation to (010) surface, except for Sb_2S_3 in which the free energy of (010) surface is still smaller than (001) as shown in Table 1. The reconstruction reduces the free energy; however, it remains much higher than the energy of the (100) surfaces.

In the inset of Figure 5e is shown a band energy scheme used to calculate through the work function the electron affinity χ_e . The electron affinity is a quantity more adequate for studying energy alignments at semiconductor interfaces. The calculated values of electron affinity for the different compounds and surfaces are presented in the Table 1. Two trends can be observed: First, the electron affinity systematically increases for surfaces (100), (010), and (001), in this sequence, with the exception of Bi_2S_3 , and second, the affinity is mainly ruled by the cations, i.e., Sb and Bi, as expected because the CBM is strongly constituted by p-atomic orbitals of these elements. SOC also have an important effect over the affinity, increasing about 0.2 eV for all compounds, hardening the removal of the electrons. Compared to experimental results, the averaged planar electron affinity of Sb_2S_3 is 4.27 eV, in good agreement with 4.25 eV reported by photoelectrons methods.⁵² Thus, on the basis of the simple concepts of the Anderson rules⁵⁹ for the energy alignment of heterostructures and using the parameters calculated in previous section, we present next the band alignment of some relevant structures based on X_2Y_3 compounds studied in this work.

Energy Band Alignment. In Figure 6a are presented energy band diagrams of interfaces between different X_2Y_3

Table 1. Surface Free Energy and the Electron Affinity for Three Different Surfaces and Four Trichalcogenides Compounds

compound	(100) surface		(010) surface		(001) surface	
	surface free energy (meV/Å ²)	electron affinity (eV)	surface free energy (meV/Å ²)	electron affinity (eV)	surface free energy (meV/Å ²)	electron affinity (eV)
Sb_2S_3	5.97	4.21	21.91	4.22	22.70	4.4
Sb_2Se_3	8.60	4.16	22.69	4.35	20.82	4.46
Bi_2S_3	9.39	4.63	27.09	4.58	24.71	4.24
Bi_2Se_3	9.37	4.51	24.81	4.59	20.17	4.61

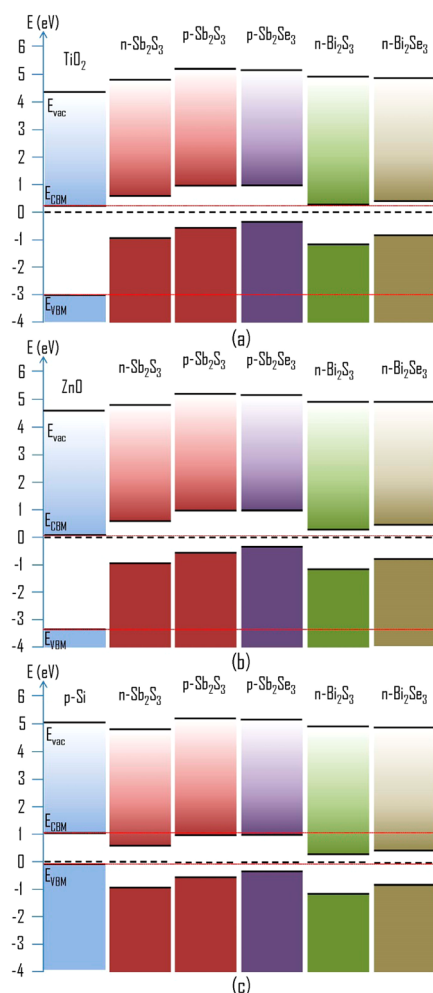


Figure 6. Band alignment of trichalcogenides at interfaces with usual photovoltaic substrates (a) TiO_2 , (b) ZnO , and (c) p-silicon.

compounds aligned to a TiO_2 substrate with Fermi level at 0.2 eV below CBM, electron affinity of 4.1 eV, and band gap of 3.2 eV, values obtained from refs 60 and 61. The Fermi energy for X_2Y_3 compounds were obtained from the defects calculations (Figure 4), taking defects with smaller formation energy and shallow levels. The electron affinity of surface (100) was used. In the diagram, one can see that only type II staggered junctions should occur between TiO_2 and X_2Y_3 . The best CBM offsets of 0.35, 0.77, and 0.78 eV are obtained for interfaces with n- Sb_2S_3 , p- Sb_2S_3 , and p- Sb_2Se_3 , respectively. However, in the case of Sb_2S_3 , a small Schottky barrier should be expected because of the larger electron affinity differences, which could compromise the performance of the junction; for Sb_2Se_3 , the Schottky barrier should be smaller. In the case of Bi-based chalcogenides because of the shallow n-type defect doping, no larger CBM offset than 0.2 eV can be obtained. These results have excellent concordance with ref 24, besides the fact that in this work no defect analysis was taken into account.

In Figure 6b, the band diagrams are aligned to a ZnO substrate with band gap of 3.4 eV, electron affinity of 4.5 eV, and Fermi level in the CBM, with values obtained from refs 52 and 62. In this case, Schottky-like barriers are only expected for junctions with n- Bi_2S_3 in which the CBM offset is negligible. The CBM offset at the interface can reach almost 1 eV for p-type Sb_2S_3 and Sb_2Se_3 , i.e., for samples grown under Sb-rich conditions. In Figure 6c, for a p-Silicon substrate, the n-type

trichalcogenides show better prospects, such as the Bi-based compounds where the Bi_2S_3 shows a VBM offset of about 1.0 eV.

Taking junctions between X_2Y_3 compounds, some interesting features could be found, as shown in Figure 7. In Figure 7a, a

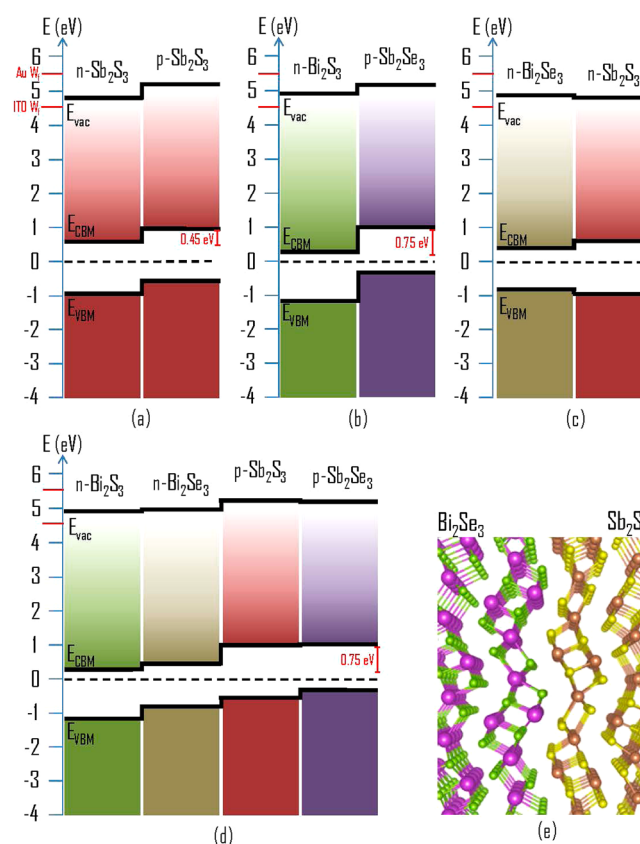


Figure 7. Band energy alignment of (a) an homojunction of Sb_2S_3 , (b) heterojunction between n- Bi_2S_3 and n- Sb_2S_3 , and (c) a type-I heterojunction formed by n- Bi_2Se_3 and n- Sb_2S_3 . (d) Trichalcogenide multijunction and (e) representation of the atomic structure of an interface between Bi_2Se_3 and Sb_2S_3 along the planes (100).

junction formed by p- and n-type Sb_2S_3 (homojunction) is displayed, with CBM offset of 0.45 eV. This kind of structure can be grown by controlling the synthesis equilibrium conditions, as described before, resulting in p–n junctions. The main advantage of such a junction is the absence of impurities needed to change the carrier type, reducing the amount of recombination centers. In Figure 7b, a heterojunction of n- Bi_2S_3 and p- Sb_2Se_3 where a high CBM offset of about 0.75 eV is found could lead to large open-circuit voltages in solar cells based on this type-II structure. However, both Bi_2S_3 and Sb_2Se_3 present similar band gaps, limiting the range of solar spectrum being absorbed and consequently the efficiency. To balance this disadvantage, Bi_2S_3 has a much higher electron affinity than Sb_2Se_3 (Table 1), which excludes the possibility of Schottky-like barrier formation that could deteriorate the solar cell.

Type-I straddling junctions can be obtained by connecting X_2Y_3 materials, as presented in Figure 7c. Straddling junctions occur when VBM and CBM of the semiconductor with smaller band gap are positioned between the VBM and CBM of the semiconductor with larger band gap. The junction between n- Bi_2Se_3 and n- Sb_2S_3 has the characteristic energy band diagram

for the construction of quantum wells. However, because of the small difference in band gap seen in Figure 7c; no VBM and CBM offsets higher than 0.18 and 0.12 eV, respectively, should be expected. With respect to this, the engineering of the band gap of these compounds could lead to interesting structures for optoelectronic application.

To improve the heterojunction shown in Figure 7b, layers of Bi_2Se_3 and Sb_2S_3 could be inserted in the middle of the Bi_2S_3 and Sb_2Se_3 structure, forming a multijunction system as presented in Figure 7d. These new layers will increase the spectral absorption of the structure because Bi_2Se_3 and Sb_2S_3 present a red- and blue-shifted band gap, respectively, in relation to those of Bi_2S_3 and Sb_2Se_3 . Still, the introduction of such layers should not destroy the staggered order, forming a stair-structured CBM, as can be seen in Figure 7d.

The utilization of a multijunction fully based on X_2Y_3 has important advantages, such as the possibility of epitaxial growth along [100] direction, the atomic structure shown in Figure 7e, where no defects are expected suppressing recombination centers and leading to high open-circuit voltages as well as high efficiencies because of a broad spectral absorption. Still, these kind of cells should presents lower costs and more easy fabrication compared to those of, for example, Ge–Ga-based n-type multijunctions.¹

The validation of Anderson model for band alignment can be assumed by comparing the results in Figure 6a with other full first-principle calculations.²⁴ The methodology employed here has equal prediction power than those based fully on atomistic first principle calculation^{24,63} and further advantages such as taking into account the existence of pinning level and intrinsic dopants, leading to more realistic results because these defects cannot be avoided in the experimental situation. Another motive is to bypass the band gap calculation, which is an inevitable issue of DFT method.

CONCLUSIONS

On the basis of first-principle calculations, we have shown that the electrical properties of the trichalcogenides X_2Y_3 are mainly ruled by point defects that generate deep electronic levels inside the band gap. The most abundant defect depends on the synthesis condition; however, in general antisites present low formation energy and transition levels closer to the band gap edges. The conduction type found experimentally was also well-explained by our calculations, showing that only Sb_2S_3 can show intrinsically n- and p-type behavior. Using slabs calculations, we obtained the work function and the electron affinity for the X_2Y_3 materials, making it possible to estimate the energy band alignment of heterostructures based on these compounds. The alignment analysis showed that Sb-based trichalcogenides better fit as an absorber in junctions based on n-type semiconductors substrates, such TiO_2 and ZnO , leading to higher CBM offset and consequently higher open-circuit voltage in solar cells. The Bi-based compounds showed the best performance when joining to hole conductors, such as p-silicon. In a last analysis, we proposed the construction of homojunctions and heterojunctions fully based on X_2Y_3 because they share the same crystalline structure with a small mismatch of lattice parameters and the possibility of growing along the (100) planes with the stacking of van der Waals separated layers where a vanishing amount of defects is expected. We showed that homojunctions of Sb_2S_3 can be obtained by simple control of the synthesis environment whereas heterojunctions of Bi_2S_3 and Sb_2Se_3 showed the

highest CBM offset among all combinations. A last proposal, looking for an improvement in the spectral absorption of the $\text{Bi}_2\text{S}_3/\text{Sb}_2\text{Se}_3$ heterojunctions, was inserting layers of the compounds Bi_2Se_3 and Sb_2S_3 in between Bi_2S_3 and Sb_2Se_3 heterojunctions, which should not destroy the stair-structured band structure and will increase the light absorption because of the dispersion of the band gaps such as in multijunction cells or tandem cells and leading to solar cells with higher open-circuit voltages and higher efficiencies. Our results can be used as guide for improvement and development of ultimate solar cells based on trichalcogenides because the electrical and electronic phenomena were fully discussed and unraveled.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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