Optical properties of Sb(Se,Te)I and photovoltaic applications

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Abstract

SbXI (X=Se, Te) are ferroelectric semiconductors that allow a variety of applications including optoelectronic and photovoltaic applications. An analysis of the optical properties is carried out starting from first-principles density-functional theory with orbital-dependent one-electron potentials. To go into the contributions to the optical properties more deeply, the absorption coefficients have been split into inter- and intra-species contributions and into atomic angular momentum contributions. The optical results are used to evaluate the efficiencies when this material is used to absorb sunlight at several sunlight concentrations and the usual radiative and the ferroelectric photovoltaic mechanisms. The results indicate their applicability in photovoltaic devices as absorbent of the solar spectrum with high conversion efficiency.

Keywords: Optical properties, Semiconductors, Efficiency, Multi-gap

1. Introduction

Ferroelectric (FE) materials display spontaneous electric polarization and have extensive potential technological applications because of the possibility of coupling the FE response to other properties. An important discovery was the highly photosensitive photoconducting ferroelectrics of SbSI [1,2]. Research into the photorefractive effect has led to the discovery of a new mechanism for charge generation in FE, the

anomalous photovoltaic effect. The FE-PV effect is observed in materials with no centre of symmetry, and several mechanisms responsible for this effect have been described [3,4]. Therefore a photoferroelectric crystal could be a possible solar energy converter. SbSI is a good candidate material for exhibiting both bulk and poly-crystalline photoferroic effects.

Just like any other type of PV device, FE materials should be able to absorb as much sunlight as possible to have a reasonably large photocurrent, which requires the FE materials to have a low band-gap and large absorption coefficient. However, SbSI exhibits an optical band-gap of $E_g \sim 2$ eV, larger than the optimum for obtaining the maximum efficiency ($\sim 41\%$ at $E_g = 1.1$ eV and at the highest sunlight concentration = 46200 sun, where 1 sun = 1 kW/m^2 , and $\sim 31\%$ at $E_g = 1.3$ eV for 1 sun) [5-8]. However this value can be tuned by the choice of chalcogen and halide. Furthermore the effective masses of the charge carriers in these materials suggest high mobility with good quality crystals with low defect concentrations [9]. It is also important to identify materials with properties similar to the hybrid perovskites (i.e. light absorption, conductivity, dynamic polarisation, and ease of manufacture), but where Pb is replaced by a more sustainable element.

For these reasons we focus our study on SbXI (X=Se,Te) with lower band-gaps than SbSI, and therefore, closer to the optimums for solar cells. Usually, as a first approximation, only the energy band-gap is considered. However the main property related to the solar spectrum absorption is the absorption coefficient. Therefore a microscopic understanding of the absorption of these materials is essential.

Here we will analyze the optical properties using first-principles. The results will be compared with theoretical and experimental data in the literature. The application of these materials to solar cells will be evaluated from the theoretical absorption

coefficients. Understanding and quantifying the interplay between the microscopic properties and the macroscopic efficiencies in the solar energy conversion will provide a major challenge for scientists and engineers in this field.

2. Calculations

The electronic and optical properties have been obtained from first principles based on the density functional theory (DFT) [10,11] with an effective on-site Coulomb U (DFT+U) factor in order to avoid DFT the self-interaction problem partially [12-16]. U depends on the choice of the orbitals on which the correction is applied, on the way the orbital occupations are computed, and on the DFT+U implementation chosen [13-16]. In this work we have used the DFT+U methodology and implementation described in references [13,14]. For the exchange-correlation potential, we use the generalized gradient approximation (GGA) from Perdew, Burke and Ernzerhof [17]. The standard Troullier–Martins [18] pseudopotentials are adopted and expressed in the Kleinman–Bylander [19] form. The valence wave functions are expanded into a numerically localized pseudoatomic orbital basis set [20]. In all results we use periodic boundary conditions, spin polarization, double-zeta with polarization localized basis sets, and the orthorhombic *Pnma* and triclinic *P-1* crystal structures with 100 and 180 special k-points in the irreducible Brillouin zone for SbSeI and SbTeI respectively. The electronic structure calculations were carried out by relaxing all the cell atoms using the conjugated gradient algorithm to minimize the calculated quantum mechanical forces. Relaxation at the absolute energy minimum is considered as accomplished when the forces on the atoms fall below $0.004 \text{ eV} \cdot \text{\AA}^{-1}$.

The optical properties have been determined on the independent-particle approximation from the complex dielectric function via the Kramers-Kronig relationship.

3. Results and discussion

3.1. Structure and electronic properties

The crystalline structure of SbSeI is orthorhombic (space group $Pnma$, n° 62) with lattice parameters $(a,b,c) = (8.698, 4.127, 10.412) \text{ \AA}$, whereas for the SbTeI is triclinic (space group $P-1$, n° 2), with $(a,b,c) = (7.570, 7.159, 4.228) \text{ \AA}$, and $(\alpha, \beta, \gamma) = (107.22, 106.18, 77.19)^\circ$. These structures (Figure 1) are built up from infinite weakly linked ribbons $(SbX_2)_n$ of trigonal SbX_3 with Sb-X bonds of 2.605, 2.795 $\text{\AA}$ (X =Se), and 2.829, 2.953, 2.955 $\text{\AA}$ (X =Te) [21]. The SbSeI experimental band-gap reported in the literature is 1.66 eV [22] and the theoretical band-gaps are between 1.29-1.40 eV (1.29 eV [9], 1.37 eV [23], 1.40 eV [24]). For SbTeI the theoretical band-gaps are 0.86 eV [24] and 2.07 eV [25].

In this work we applied the orbital-dependent one-electron potential using the DFT+U formalism described in references [13-14]. The band-gaps obtained for X=Se with $U=0$ eV, $U= 3$ eV are 1.41 eV and 1.75 eV. Because of the well-known tendency of DFT calculations to underestimate the band-gap, the value with $U=0$ underestimates the band-gap with respect to the experimental. This value is similar to other previous results in the literature [23,24]. However, including an effective Hubbard $U=3$ eV in the Hamiltonian, the band-gap is closer to the experimental. For X=Te the band-gaps with $U=0/3$ eV are 0.68/1.05 eV.

In order to determinate the atomic and orbital composition of the band edges we have calculated the projected density of states (PDOS) as a function of energy. From the results shown in Figure 2, the states of the VB edge are derived mainly from $p(I)+p(Se)$, and with lower proportion from $p(Sb)$ states. The CB edge states consist mainly of the $p(Sb)$, and with lower proportion from $p(I)\sim p(Se)$ states. These results are in accordance with other results in the literature [9].

3.2. Optical Properties

The joint DOS is often used to analyze the optical transitions. However, to use the joint DOS is an oversimplification. The joint DOS is obtained not considering the momentum operator matrix elements, i.e. taking all equal to unity. For instance, when an atom or a group of atoms makes a larger contribution to the band edge states, it does not necessarily mean that they contribute significantly to the optical properties. The contribution depends on both, the joint DOS and the momentum operator matrix elements. If one is large but not the other, the contribution will be very small. For this reason a splitting of the absorption coefficients into inter- and intra-species contributions α^{AB} and into angular momentum contributions $\alpha_{l_A l_B}^{AB}$ should always be considered.

From the electronic results and with the additional calculation of the momentum operator matrix elements $p_{\mu\lambda}$ we have obtained the absorption coefficients according to what is described in the calculation section. Nevertheless, in order to quantify the contributions from the chemical species, we have split the absorption coefficients taking in account that the optical properties depend on the square of $p_{\mu\lambda}$. It can be split into species contributions: $p_{\mu\lambda} = \sum_A \sum_B p_{\mu\lambda}^{AB}$, where $p_{\mu\lambda}^{AB}$ is the inter-species component that couples the basis set functions on different species atoms, A and B. If A=B, it represents an intra-species component. Then, the absorption coefficients and other optical properties can be split: $\alpha = \sum_A \sum_B \alpha_{AB} +$ (terms involving three and four different non-equivalent species). The results from this splitting are shown in Figures 3 and 4 (a panels). The largest contribution is from $\alpha_{\text{Sb,Sb}}$, and with lower proportion from $\alpha_{\text{Se,Se}}$, $\alpha_{\text{I,I}}$, $\alpha_{\text{Se,Sb}}$, and $\alpha_{\text{I,Sb}}$. The other transitions, not shown in the Figures, make a very low contribution. This analysis is in agreement with the previous PDOS.

To look at the contributions from the atomic states in more detail, $p_{\mu\lambda}^{AB}$ can additionally be split into atomic angular momentum contributions like $p_{\mu\lambda}^{AB} = \sum_{l_A} \sum_{l_B} (p_{\mu\lambda}^{AB})_{l_A l_B}$, where $(p_{\mu\lambda}^{AB})_{l_A l_B}$ is the contribution of the transition between the l_A shell-states (in A) and the l_B shell-states (in B). Then the absorption coefficient can be split as $\alpha = \sum_A \sum_B \sum_{l_A \in A} \sum_{l_B \in B} \alpha_{l_A l_B}^{AB} + (\text{terms involving three and four different non-equivalent species})$. When the absorption coefficients are split into atomic angular momentum contributions, the more important $\alpha_{l_A l_B}^{AB}$ contributions to the absorption coefficient are represented in Figures 3 and 4 (b panels). The main contribution is from α_{sp}^{SbSb} and with a lower proportion from α_{sp}^{SeSe} , α_{sp}^{II} , α_{pp}^{SeSb} and α_{pp}^{ISb} . As usual we use the notation s, p, d , etc for $l=0, 1, 2$, etc.

Note that the intra-species transitions include all transitions between states of the atoms of the same specie (identical and symmetrically equivalent atoms). It includes intra-atomic and inter-atomic transitions involving mono-centric and bi-centric matrix elements respectively. Therefore, although for atoms the (intra-atomic) transitions between states with equal angular momentum l are forbidden, the inter-atomic transitions between atoms located at different sites can be allowed. It is because of that the translation of a regular lm -solid harmonic gives a finite expansion of regular $\lambda\mu$ -solid harmonics with λ from 0 to l and with μ from $-\lambda$ to λ [26]. As a consequence, the transition selection rules are determined by the system (atomic, molecular, solid) symmetry [27]. Therefore, depending on the symmetry, the intra-specie transitions between states with equal angular momentum may be allowed, unlike what happens in atoms. The same applies to the inter-species transitions.

According with the PDOS the largest contributions to the transition came from the $[p(I)+p(Se)]_{VB} \rightarrow [p(Sb)]_{CB}$ transitions. However the splitting of the absorption

coefficients indicate that the main contributions came from the $\alpha_{\text{Sb,Sb}}$ intra-species contribution and from $\alpha_{sp}^{\text{SbSb}}$ angular momentum contribution. This difference is because both, the joint DOS and the momentum operator matrix elements between the Sb-Sb atoms and the s(Sb) and p(Sb) states are larger. Therefore, as it has been mentioned previously, a splitting of the absorption coefficients into inter- and intra-species contributions α^{AB} and into angular momentum contributions $\alpha_{l_A l_B}^{AB}$ should always be considered because the joint DOS is an oversimplification.

3.3. Solar cell efficiencies

In order to estimate the potentiality of Sb(Se,Te)I as a solar-cell device, we have obtained (Figure 5) the maximum efficiency, assuming the usual approximations [5-8], except that the cell absorbs all incident photons above the band-gap E_g . It implicitly implies that the absorption coefficients are a step function (0 for $E < E_g$ and a constant for $E \geq E_g$). Then the efficiency is determined mainly by the band-gap energy. With this approximation the maximum efficiencies are approximately 31 % and 41 % without ($f_C = 1$) and at the highest sunlight concentration ($f_C = 46200$) respectively.

This approximation, absorption coefficients as step functions, is in part due to the simplification of the calculation and the difficulty in obtaining absorption coefficients (theoretically or experimentally) with respect to the energy band-gap. However, the absorption depends on the absorption coefficient. We have used the absorption coefficients obtained from first-principles instead of step functions. Then the efficiencies also depend on the thickness w of the device (Figure 5). From the figure, solar cell devices based on Sb(Se,Te)I, a few microns thick, could reach efficiencies close to the maximum efficiencies: ~28(29) % without sunlight concentration ($f_C = 1$),

and ~34(39) % with the maximum concentration factor $f_c = 46200$ for $X=\text{Se}(\text{Te})$. It indicates a huge potentiality as solar cell absorbers of the solar spectrum.

So far we have considered the traditional radiative PV effect (R-PV) on single-gap semiconductors. There are alternatives to increasing the limiting efficiency of single-gap solar cells. Here we consider two possibilities: (i) an alternative in FE materials is to take advantage of the FE-PV effect [3,4], an additional mechanism for generating photocurrent in FE semiconductors. In this case the current generation is due to the FE polarization instead of radiative optical transitions with the R-PV mechanism; (ii) to increase the absorption of the solar spectrum with multi-gap semiconductors with intermediate bands between the traditional valence band and conduction band.

When the R-PV effect coexist with other mechanism for generating photocurrent the maximum voltage will be limited by the band-gap and the maximum current corresponds to suppressing the emitted radiative current completely. With these conditions the efficiencies for $X=\text{Se}(\text{Te})$ are ~39(44) % using the band-gaps 1.7 (1.0) eV respectively. The FE-PV effect only slightly increases the potentiality of the FE material with respect to the R-PV with maximum concentration. In any case the coexistence of radiative and ferroelectric photovoltaic effects increase the efficiency of any of the mechanisms separately. However, for any mechanism or combination of photovoltaic mechanisms the output power of a solar cell is limited by the amount of power absorbed from the radiation due to the energy conservation. The power absorbed depend on the absorption coefficient. Any mechanisms exploit only a fraction of this power absorbed. Therefore, the previous results correspond with the maximum efficiency for any mechanism or combination of photovoltaic mechanisms that are able to exploit the full power absorbed by the semiconductor.

With multi-gap semiconductors both the current and the efficiency are increased [5-8]. Using the theoretical band-gaps the efficiencies with maximum concentration are approximately 54 (64) % and 55 (70) % from double- to triple-gap solar cells respectively. From the double-gap (3 bands) these values exceed the limits of the single-gap solar cell when the traditional R-PV effect coexists with other mechanism.

In addition to the properties of the absorbent material, the real efficiency depends on the architecture of the solar cell, the contacts, etc. Nevertheless, the maximum efficiency is a criterion to evaluate the potentiality as a solar cell: if it is small the material is not a good candidate for absorbing solar radiation.

4. Conclusions

Using GGA+U first-principles density-functional theory we have studied the electronic and optical properties of the SbXI (X=Se, Te). Our theoretical results are in accordance with previous theoretical and experimental results in the literature. The absorption coefficients have been obtained and analyzed in depth. They have been split into inter- and intra-species contributions and into atomic angular momentum contributions. The largest contributions to the optical properties are from the s(Sb)-p(Sb) transitions.

The potentiality as sunlight absorbent in single-gap solar cell has been evaluated from the theoretical absorption coefficients. An Sb(Se,Te)I solar cell, a few microns thick, could reach efficiencies close to the maximum efficiencies. Because of their ferroelectric properties, there is an additional mechanism to generate photocurrent: the FE-PV effect. The potential as a single-gap solar cell has been evaluated considering the combination of both R-PV and FE-PV effects. The FE-PV effect only slightly increases the potentiality of the FE material with respect to the R-PV effect with maximum

concentration. In order to increase the efficiency it is necessary to increase the absorption of the solar spectrum with multi-gap semiconductors.

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References

- [1] E. Fatuzzo, G. Harbeke, W. J. Merz, R. Nitsche, H. Roetschi and W. Ruppel, *Phys. Rev.*, **127** (1962) 2036–2037.
- [2] R. Nitsche, H. Roetschi and P. Wild, *Appl. Phys. Lett.*, **4** (1964) 210–211.
- [3] Belinicher V. I. and Sturman B. I., The photogalvanic effect in media lacking a center of Symmetry, *Sov. Phys. Usp.* **23** (1980) 199-223.
- [4] Fridkin V. M., *Photoferroelectrics*, Springer-Verlag Berlin Heidelberg New York 1979.
- [5] A. Luque and A. Martí, Theoretical Limits of Photovoltaic Conversion, in *Handbook of Photovoltaic Science and Engineering* Edited by A. Luque and S. Hegedus, John Wiley & Sons Ltd (2003).
- [6] P. Würfel, *Physics of Solar Cells. From Principles to New Concepts*, 2005 WILEY-VCH Verlag GmbH & Co, KGaA.
- [7] M.A. Green, *Third Generation Photovoltaics. Advanced Solar Energy Conversion*, Springer-Verlag Berlin Heidelberg 2003, 2006.
- [8] A. S. Brown and M. A. Green, *J. Appl. Phys.*, **92** (2002) 1329-1336.
- [9] K. T. Butler, J. M. Frost and A. Walsh, Ferroelectric materials for solar energy conversion: photoferroics revisited, *Energy Environ. Sci.*, **8** (2015) 838.
- [10] W. Kohn and L. J. Sham, Self-Consistent Equations Including Exchange and Correlation Effects, *Phys. Rev.* **140** (1965) A1133-A1138.
- [11] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejon, and D. Sánchez-Portal, The SIESTA Method for Ab initio Order-N Materials Simulation, *J. Phys.: Condens. Matter* **14** (2002) 2745-2779, and references therein.
- [12] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Band Theory and Mott Insulators: Hubbard U instead of Stoner I, *Phys. Rev. B*, **44** (1991) 943-954; V. I. Anisimov, I. V.

- Solovyev, and M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Density-Functional Theory and NiO Photoemission Spectra, *Phys. Rev. B* 48 (1993) 16929–16934.
- [13] C. Tablero, Representations of the Occupation Number Matrix on the LDA/GGA+U Method, *J. Phys.: Condens. Matter* 20 (2008) 325205.
- [14] C. Tablero, Effects of the Orbital Self-interaction in both Strongly and Weakly Correlated Systems, *J. Chem. Phys.* 130 (2009) 054903.
- [15] D. D. O'Regan, M. C. Payne, and A. A. Mostofi, Subspace Representations in Ab initio Methods for Strongly Correlated Systems, *Phys. Rev. B* 83 (2011) 245124.
- [16] M. Grisolia, P. Rozier, and M. Benoit, Density Functional Theory Investigations of the Structural and Electronic Properties of Ag₂V₄O₁₁, *Phys. Rev. B* 83 (2011) 165111.
- [17] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* 77 (1996) 3865-3868.
- [18] N. Troullier and J. L. Martins, Efficient Pseudopotentials for Plane-wave Calculations, *Phys. Rev. B* 43 (1991) 1993-2003.
- [19] L. Kleinman and D. M. Bylander, Efficacious Form for Model Pseudopotentials, *Phys. Rev. Lett.* 48 (1982) 1425-1428; D. M. Bylander and L. Kleinman, 4f Resonances with Norm-conserving Pseudopotentials, *Phys. Rev. B* 41 (1990) 907-912.
- [20] O. F. Sankey and D. J. Niklewski, Ab initio Multicenter Tight-binding Model for Molecular-dynamics Simulations and Other Applications in Covalent Systems, *Phys. Rev. B* 40 (1989) 3979-3995.
- [21] A. Ibanez, J. Jumas, J. Olivier-Fourcade, E. Philippot, M. Maurin, Sur les Chalcogeno-iodures d'antimoine SbXI (X=S,Se,Te): Structures et spectroscopie Moessbauer de ¹²¹Sb, *J. Solid State Chem.* 48 (1983) 272-283.
- [22] O. M. Madelung, *Semiconductors: Data Handbook*, Springer, Berlin, 3rd edn, 2004.

- [23] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder and K. A. Persson, Commentary: The Materials Project: A materials genome approach to accelerating materials innovation, *APL Materials* 1 (2013) 011002; S. P. Ong, W. D. Richards, A. Jain, G. Hautier, M. Kocher, S. Cholia, D. Gunter, V. L. Chevrier, K. A. Persson and G. Ceder, Python Materials Genomics (pymatgen): A robust, open-source python library for materials analysis, *Comput. Mater. Sci.* 68 (2013) 314.
- [24] E. Saal, S. Kirklin, M. Aykol, B. Meredig, and C. Wolverton, Materials Design and Discovery with High-Throughput Density Functional Theory: The Open Quantum Materials Database (OQMD), *JOM* 65 (2013)1501-1509.
- [25] W. Setyawan, R. M. Gaume, S. Lam, R. S. Feigelson, and S. Curtarolo, High-Throughput Combinatorial Database of Electronic Band Structures for Inorganic Scintillator Materials, *ACS Combinatorial Science* 13 (2011) 382-390.
- [26] J. Fernández Rico, R. López, I. Ema and G. Ramírez, Translation of real solid spherical harmonics, *Int. J. Quantum Chem.* 113 (2013) 1544–1548.
- [27] M. Lax, *Symmetry Principles in Solid State and Molecular Physics*. Dover Publications, Mineola, New York 2012.

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Figure 1: The SbXI crystalline structures with (a) X=Se and (b) X=Te.

Figure 2: Projected density of states on the main shell atom states for the SbXI with (a) X=Se and (b) X=Te. The VB edge has been chosen as the origin of the energy. The positive (negative) values correspond to the spin up (down) components.

Figure 3: More important absorption coefficients split into (a) chemical species contributions α_{AB} and (b) angular momentum contributions $\alpha_{l_A l_B}^{AB}$ for SbXI with X=Se.

Figure 4: Same legend as in Fig. 3, but for X=Te.

Figure 5: Efficiency η (%) as a function of the cell thickness w using the absorption coefficients obtained from calculations. The fine and thick lines correspond to the light concentration factor $f_c = 1$ (without concentration) and the maximum concentration ($f_c = \text{max} \sim 46200$) for SbXI with X=Se, Te.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5