The optoelectronic properties of a solar energy material: Ag$_2$HgSnS$_4$

S Hadjri Mebarki, B Amrani, K Driss Khodja and A Khelil

University d'Oran Ahmed Ben Bella, Laboratoire des Couches minces et Matériaux pour l'Electronique, BP 1524 El Mnaouer Oran, Algeria

Email: abouhalouane@yahoo.fr

Abstract. We used an ab initio full potential-linearized augmented plane wave technique within the density functional theory to study the structural and optoelectronic properties of Ag$_2$HgSnS$_4$ in a wurtzite-stannite phase. The exchange correlation effects are included through the generalized gradient approximation and modified Becke-Johnson exchange potential. Various physical quantities, such as lattice parameter, bulk modulus, band structure and density of states, are given. Also, we have presented the results of the effective mass for the electrons in the CB and the holes in the BV. We show that the modified Becke-Johnson exchange potential can predict the energy band gap in better agreement with the experiment. In addition the dielectric function and energy-loss function are presented for the energy range of 0-26 eV. The electronic and optical properties indicate that this compound can be successfully used in optoelectronic devices

1. Introduction

Ag$_2$HgSnX$_4$ where X=S or Se, and related compounds have attracted increased attention over the past few years due to their variety of applications in optoelectronics and non-linear optics devices, owing to their n-type conductivity, high absorption coefficient, suitable band gap, lower cost and environmental compatibility [1-19].

The quaternary sulfide (Ag$_2$HgSnS$_4$) exists in the quasitermary Ag$_2$S–HgS–SnSe system [20, 21]. For the first time it was synthesized by Haeuseler and Himmrich [22] using the solid state reactions at 970 K. It was ascertained that the sample of Ag$_2$HgSnS$_4$ crystallizes into a wurtzite–stannite (space group Pmn$_2$1) structure with the lattice parameters $a = 8.203$, $b = 7.026$, and $c = 6.710$ Å. Its Far-infrared and Raman spectra was studied by the same authors [23]. Parasyuk et al. [21] have reported measurements of the absorption edge in Ag$_2$HgSnS$_4$ lead to estimates of the bandgap energy $E_g$ from liquid nitrogen temperature to room temperature. Recently, Bozhko et al. [24] have used XPS method to measure the binding energies of core-level electrons of atoms constituting Ag$_2$HgSnS$_4$.

A deeper knowledge of its properties would help improve the understanding of this compound and stimulate the development of new applications.

To the best of our knowledge there are no theoretical calculations exploring the optoelectronic properties of this compound. Consequently, the primary purpose of this work is to provide some additional information to the existing data on the physical properties of Ag$_2$HgSnS$_4$ by using the full-potential linearized augmented plane wave method. After introducing the problem, the remaining
paper is organized as follows: in Section 2, we describe the calculation procedure. Results are presented in Section 3. Section 4 contains the conclusion.

2. Method of calculations
The first-principles calculations performed in this paper are based on the density functional theory (DFT). The total energies were calculated within the full potential linearized augmented plane wave (FPLAPW) +local orbitals (lo) method, implemented in the WIEN2k code [25]. In this code, the crystal structures were decided under the condition that the total energy is minimized from all atomic configurations. The exchange and correlation effects were treated using the generalized gradient approximation (GGA96) based on Perdew et al. [26] in the structural analysis, and modified Becke-Johnson (mBJ) as coupled with (GGA96) approach to treat the optoelectronic properties [27]. The mBJ exchange potential, as an orbital independent and semi-local exchange correlation potential, has been proved to yield quite accurate gaps for numerous semiconductors [28, 29, 30]. The sphere radii used in the calculations for Ag, Hg, Sn and S are 2.46, 2.5, 2.26 and 1.85 u.a., respectively. Within these spheres, the potential is expanded in the form

\[
V(r) = \sum_{lm} V_{lm}(r) Y_{lm}(\hat{r})
\]

and outside the sphere,

\[
V(r) = \sum_{\mathbf{k}} V_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}
\]

where \( Y_{lm}(\hat{r}) \) is a linear combination of radial functions times spherical harmonics. Within this calculational scheme, there are no shape approximations to the charge density or potential. Special attention has been paid to the convergence of the total energy with respect to the cut off. In consideration of computational cost, we choose the Brillouin-zone sampling mesh parameters for the \( k \)-point set are 27.

3. Results and discussion

3.1. Structural properties
The structure parameters for wurtzite-stannite phase from experimental observations [21, 22] were optimized and then listed in table 1. The calculated total energies were fitted to the Murnaghan [31] equation of state. Compared with the experimental results, the theoretical lattice parameters \( a, b, \) and \( c \) are larger with relative errors of 1.58%, 2.38 and 2.32%, respectively. Thus, the theoretical results of our calculations are credible. The bulk modulus \( (B_0) \) and its pressure derivative \( (B_0') \) are obtained. Unfortunately, no experimental data are yet available to compare with the present calculated results.

| Approach    | \( a_{eq} \) Å | \( b_{eq} \) Å | \( c_{eq} \) Å | \( B_{eq} \) (GPa) | \( B' \) |
|-------------|----------------|----------------|----------------|-------------------|-------|
| This work   | 8.333          | 7.193          | 6.866          | 46.171            | 4.596 |
| Experiment  | 8.207<sup>a</sup> 7.033<sup>b</sup> 6.718<sup>a</sup> | 8.203<sup>b</sup> 7.026<sup>b</sup> 6.710<sup>b</sup> |
|<sup>a</sup>Ref. [21] |<sup>b</sup>Ref. [22] |

3.2. Electronic properties
The band structures of Ag<sub>2</sub>HgSnS<sub>4</sub>, calculated by using the FP-LAPW approach and GGA, are shown in Figure. 1a. This figure shows that the wurtzite-stannite phase is a direct band gap semiconductor.
The conduction band minimum located at the \( \Gamma \)-point and the valence band maximum is located close to the \( \Gamma \)-point resulting in a direct band gap of 0.109 eV. This value is much smaller than the experimental result determined by Parasyuk [21]. It is well known that band structure calculations based on the GGA method underestimate the band gap, due to its incomplete cancellation of the self-interaction. There is an overall topological resemblance of the present band structure and those calculated by Dan and Hing-Hong [32]. In order to improve the band gap prediction of \( \text{Ag}_2\text{HgSnS}_4 \), the modified Becke–Johnson exchange–correlation potential was also used. It is clear from the figure 1b, that the calculated band gap with mBJ 1.21 eV is consistent with the experimentally reported result of 1.32 eV [21].

![Figure 1](image1.png)

**Figure 1.** Band structures calculated for \( \text{Ag}_2\text{HgSnS}_4 \). Band structures using (a) GGA (b) and mBJ. The energy zero is taken at \( E_f \).

Figure 2 shows the partial density of state (PDOS) together with the total DOS of \( \text{Ag}_2\text{HgSnS}_4 \), and we can distinguish two important valence band regions, which we call for simplicity VB1 and VB2 from the top of the valence bands. We find a lower valence bands (VB2 at 7.31-5.94 eV below the Fermi energy \( E_f \)) that are formed by Sn \(-s\) and S \(-s\) states, and the main contributions is from the S \(-s\) states. The upper valence bands VB1 are formed by \( \text{Ag} \)-\( -d\) with some admixture of Hg \(-d\) and Sn \(-s\ p\) states. The conduction band is formed mainly by Sn \(-p\). These results are in good agreement with XPS method of Bozhko et al. [24].

![Figure 2](image2.png)

**Figure 2.** Calculated total density of states of \( \text{Ag}_2\text{HgSnS}_4 \). Fermi level is set at zero energy.
Turning to the effective masses, we are interested to study the effective masses of electrons and holes, which are important for the excitonic properties. We have computed the effective masses of electrons and holes both at the conduction-band minima and valence-band maxima. The corresponding values are 0.492 $m_0$ and 1.151 $m_0$ for electron and hole, respectively.

3.3. Optical properties

It is known that the optical properties of a medium can be depicted well by frequency dependent complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. In order to calculate related dielectric tensor, improved tetrahedron scheme [33] is applied for the BZ integration as provided in WIEN2k package. The imaginary part $\varepsilon_2(\omega)$ was carried out by calculating the electronic structure, using the joint density of states and the optical matrix elements. The real part of dielectric tensor $\varepsilon_1(\omega)$ was obtained from $\varepsilon_2(\omega)$ using Kramers-Krönig relationship. For detail description of this approach used for the calculation of optical properties, work of Ambrosch-Draxl and Sofo will be very helpful [34].

To the best of our knowledge, no theoretical calculations exploring the optical properties have yet been made of Ag$_2$HgSnS$_4$. Hence our work is a first attempt in this direction. Using the method above, we have calculated the imaginary $\varepsilon_2(\omega)$ and real $\varepsilon_1(\omega)$ parts for Ag$_2$HgSnS$_4$ and the results are shown in figure 3. Our dielectric functions show that the threshold peak appears at 1.21 eV. This energy is related to direct transition between the absolute fourth valence band maximum and the first conduction band minimum $\Gamma_v-\Gamma_c$. All the band transitions which contribute to the structures of $\varepsilon_2(\omega)$ are primarily from Ag $-d$ states to Sn $-p$ states. Additionally, It is clear that there is a significant anisotropy between the three spectra corresponding to different polarizations.

![Figure3. The imaginary and real parts of dielectric function of Ag$_2$HgSnS$_4$](image)

The static dielectric functions are obtained as the zero frequency limit of the real part of the frequency-dependent dielectric function. The calculated $\varepsilon_\infty$ is 5.82. We note that a smaller energy gap yields a larger $\varepsilon_\infty$ value. This could be explained on the basis of the Penn model [35]. The Penn model is based on the expression $\varepsilon_\infty \approx 1 + (h\omega_p/E_g)^2$. It is clear that $\varepsilon_\infty$ is inversely proportional to $E_g$. Hence, smaller $E_g$ yields larger $\varepsilon_\infty$.

The corresponding energy-loss function, $L(\omega)$ is presented in figure 4. The $L(\omega)$ describes the energy loss of fast electrons traversing the material. The sharp maxima in the energy loss function are associated with the existence of plasma oscillations [36]. The curves of $L$ have a maximum near 12.56 eV. This value is similar to that estimated for Ag$_2$HgSnSe$_4$ [32]
Figure 4. The electron energy loss spectrum of Ag$_2$HgSnS$_4$

4. Conclusion
Using first principles calculations, we have obtained the results of Ag$_2$HgSnS$_4$ in the wurtzite-stannite phase. Our main results and conclusions can be summarized as follows:
(i) The calculated structural properties agrees nicely with earlier reported work in the literature.
(ii) The band gap calculated show that Ag$_2$HgSnS$_4$ is a direct semiconductor with a band gap around 1.21 eV, which is in good accord with experimental value 1.32 eV.
(iii) Density of states analysis showed that the lower part of the valence bands is dominated by S -s orbital and upper part by S -s and Ag -s orbital in Ag$_2$HgSnS4.
(iv) We have computed the effective masses of the electrons and the holes.
(v) We have calculated the dynamic dielectric function. Further, we have derived the static dielectric constant. All the band transitions which contribute to the structures of $\varepsilon_2(\omega)$ are primarily from Ag $-d$ states to Sn $-p$ states. We have also presented the energy loss function.

The reported calculations provide new structural, electronic and optical results from first principles for Ag$_2$HgSnS$_4$. Hence, this study forms part of a large theoretical effort to explore the properties of this compound.

References
[1] Liu M L, Chen I W, Huang F Q, Chen L D 2009 Adv. Mater 21 p 3808.
[2] Lekse J W, Moreau M A, McNerny K L, Yeon J, Halasyamani P S, Aitken J A 2009 Inorg. Chem 48 p 7516.
[3] Uday Bhaskar P, Guresh Babu G, Kishore Kumar Y B, Sundara Raja V 2013 Thin Solid Films 534 p 249
[4] Lekse J W, Leverett B M, Lake C H, Aitken J A 2008 J. Solid State Chem 181 p 3217.
[5] Guo Q, Ford G M, Yang W C, Walker B C, Stach E A, Hillhouse H W, Agrawal R 2010 J. Am. Chem. Soc 132 p 17384.
[6] Ford G M, Guo Q, Agrawal R, Hillhouse H W 2011 Chem. Mater 23 p 2626.
[7] Rincón C, Quintero M, Moreno E, Power C, Quintero E, Henao J A, Macías M A, Delgado G E, Tovar R, Moro-coima M 2011 Solid State Commun 151 p 947.
[8] Li Y, Fan W, Sun H, Cheng X, Li P, Zhao X 2011 J. Phys. Condens. Matter 23 p 225401.
[9] Brunetta C D, Minsterman W C III., Lake C H, Aitken J A 2012 J. Solid State Chem 187 p 177.
[10] Shi X I, Huang F Q, Liu M L, Chen L D 2009 Appl. Phys. Lett 94 p 122103.
[11] Steinhagen C, Pantani M G, Akhavan V, Goodfellow B, Koo B, Korgel B A 2009 J. Am. Chem. Soc 131 p 12554.
[12] Tanaka K, Oonuki M, Moritake N, Uchiki H 2009 Sol. Energy Mater. Sol. Cells 93 p 583.
[13] Todorov T K, Reuter K B, Mitzi D B 2009 Appl. Phys. Lett 94 p 122103.
[14] Pearton S J, Abernathy C R, Norton D P, Hebart A F, Park Y D, Boatner L A, Budai J.D. 2003 Mater. Sci. Eng. R 40 p 137.
[15] Dan L, Xing-Hong Z 2011 Chin. Phys. B 20 p 126102.
[16] Ohmer M C, Pandey R 1998 MRS Bull 23 p 16.
[17] Honig H, Shen H, Yao G, Doverspike K, Kershaw R, Dwight K, Wold A 1998 Mater. Res. Bull 32 p 307.
[18] Levencso S, Duncencho D, Huang Y S, Arushanov E, Tezlevan V, Tiong K K, Du C H 2011 J. Alloys Comp 509 p 7105.
[19] Shavel A, Arbiol J, Cabot A 2010 J. Am. Chem. Soc 132 p 4514.
[20] Parasyuk O V 1999 J. Alloys Comp 291 p215.
[21] Parasyuk O V, Chykrih S I, Bozhko V V, Piskach L V., Bogdanyuk M S, Oleksiyuk I D, Bulatetska L V, Pekhnyo V I 2005 J. Alloys Comp 399 p 32.
[22] Haueseler H, Himmrich M 1989 Z. Naturforsch 44b p 1035.
[23] Himmrich M, Haueseler H 1993 Spectrochim. Acta 47A p 933.
[24] Bozhko V V, Tretyak A P, Parasyuk O V, Ocheretova V A, Khyzhun O Y 2014 Opt. Mater 36 p 977.
[25] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D, Luitz J 2001, WIEN2k, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties, Vienna University of technology, Vienna, Austria.
[26] Perdew J P, Burke S, Emzerhof M 1996 Phys. Rev. Lett. 77 p 3865.
[27] Tran F, Blaha P 2009 Phys Rev Lett 102 226401
[28] Sharma S, Verma A S, Jindal V K 2014 Mater. Res. Bull 53 p 218.
[29] Camargo-Martinez JA, Baquero R 2012 Phys. Rev. B 86 p. 195106.
[30] Khan I, Ahmad I, Rahnamaye Aliabad H A, Maqbool M 2015 Mat. Today Proc 2 p 5122.
[31] Murnaghan F D 1944 Proc. Natl. Acad. Sci. USA 30 p 5390.
[32] Dan L and Xing-Hong Z 2011 Chin. Phys. B 20 p 126102.
[33] Jepsen O and Andersen O K 1971 Solid state Commun 9 p 1763; Lehmann G and Taut M 1972 Phys. Status Solidi b 54 p 496.
[34] Ambrosch-Draxl C and Sofo J O 2006 Comput. Phys. Commun. 175 p 1.
[35] Penn D R 1962 Phys. Rev 128 p 2093.
[36] Philipp H R, and Ehrenreich H 1963 Phys. Rev. 129 p 1550.