First-Principles Study of ZnIn_2Te_4 and HgIn_2Te_4 Defect-Chalcopyrite Semiconductors Under Different Pressures: Electronic, Elastic, And Optical Properties

SATISH CHANDRA (✉ chandra.satish1989@gmail.com)

Madan Mohan Malaviya University of Technology <https://orcid.org/0000-0002-8719-1887>

V. Kumar

Indian Institute of Technology

Research Article

Keywords: first-principle calculations, defect chalcopyrite, electronic properties, Debye temperature, and optical properties

Posted Date: September 21st, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-648445/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

First-principles study of ZnIn_2Te_4 and HgIn_2Te_4 defect-chalcopyrite semiconductors under different pressures: Electronic, elastic, and optical properties

S. Chandra,^{1,*} and V. Kumar²

¹Department of Electronics and Communication Engineering, Madan Mohan Malviya University of Technology, Gorakhpur-273010

²Department of Electronics and Communication Engineering, Indian Institute of Technology (Indian School of Mines), Dhanbad-826004

*Corresponding email: chandra.satish1989@gmail.com

Abstract

First-principle calculations of electronic, elastic, and optical properties for ZnIn_2Te_4 and HgIn_2Te_4 defect-chalcopyrite semiconductors have been performed using local density approximation (LDA). Computed energy bandgaps are 1.398 eV and 1.101 eV, respectively, for ZnIn_2Te_4 and HgIn_2Te_4 , which show the indirect bandgaps behavior. Elastic parameters and Debye temperature have also been investigated at 0, 5, 10, 13, and 14 GPa pressures. Calculated results indicate that both semiconductors are covalent in nature at 0 GPa and become ionic afterward. Optical parameters have also been examined under 0, 5, 10, and 13 GPa in the energy span of 0 eV to 15 eV. The calculated values indicate that these semiconductors are mechanically stable up to 13 GPa and become unstable at 14 GPa. The Calculated values of all parameters are compared with the available experimental and reported values at 0 GPa. A reasonable agreement has been obtained between them. The values of these parameters at 5, 10, 13, and 14 GPa pressures are reported for the first time.

Keywords: first-principle calculations, defect chalcopyrite, electronic properties, Debye temperature, and optical properties.

1. Introduction

Defect-chalcopyrites (DCs) are special type of semiconductors of $A^{II}B_2^{III}C_4^{VI}$ family, which have an ordered vacancy compounds (OCV) structure. They have potential applications in the areas of solar cells, optoelectronics, linear and nonlinear optical devices [1–9]. As a result, much emphasis has been placed on the experimental synthesis and structural characterization of these materials. Experimentally, the Bridgman and chemical vapor transport (CVT) methods have been used to investigate their properties, which are observed by X-ray diffraction and Raman scattering [10–17]. Whereas theoretically, the density functional theory (DFT) has been used by different workers [2–5, 18–20]. Recently, the authors have also used the first-principle calculations to investigate the different linear properties of $LiGaS_2$, $LiGaSe_2$, $ZnGeN_2$ semiconductors [21, 22], and functionalized graphene semiconductors [23]. Various linear [24] and nonlinear optical (NLO) properties [25] of chalcopyrites have also been studied using plasma oscillations theory of solid. So far, no work has been carried out under different pressures. In this paper, we have investigated the effect of pressure on various properties of XIn_2Te_4 ($X = Hg, Zn$) defect-chalcopyrites using first-principle calculations. The effect of the pressure on C_{ij} , G , B , v , B/G ratio, A , and Θ_D parameters have been studied at 0, 5, 10, 13, and 14 GPa. The values of lattice parameter (a , c), anion displacement parameters (U_x , U_y , and U_z), bond lengths (d_{X-Te} , d_{In^1-Te} and d_{In^2-Te}), energy bandgap (E_g), and density of states (DOS) have been calculated at ambient conditions. The optical properties have also been investigated in the energy range of 0 eV to 15 eV at pressures of 0, 5, 10, and 13 GPa. The estimated values of all 23 parameters are reasonably agreed with the known experimental and theoretical data at 0 GPa. The calculated values of these parameters at 5, 10, 13, and 14 GPa pressures are reported for the first time.

2. Computational methods

First-principle calculations within DFT have been done using Cambridge Sequential Total Energy Package (CASTEP) [26] code to estimate linear properties such as electronic, optical, and elastic properties of $X\text{In}_2\text{Te}_4$ ($X = \text{Zn}, \text{Hg}$) under different pressures. The calculations are based on local density approximation (LDA) of the Ceperley and Alder scheme parameterized by Perdew and Zunger to define exchange-correlation functions [27, 28]. The non-converging pseudo-potentials [29] have been applied with 660 eV cut-off energy for the plane-wave basis set. The reciprocal crystal lattice and Brillouin zone integration have been executed using Monkhorst-pack mesh of $3 \times 3 \times 3$ within the Broyden, Fletcher, Goldfarb, and Shanno (BFGS) scheme [30]. Throughout geometry optimization, ultrafine quality for convergence threshold has been applied wherein Hell-Feynman ionic force is $0.01 \text{ eV/\AA}$, maximum total energy $5 \times 10^{-6} \text{ eV/atom}$, maximum ion displacement $5 \times 10^{-4} \text{ \AA}$, and stress tolerance 0.02 GPa .

3. Results and discussion

3.1. Structural properties

Defect-chalcopyrite semiconductors with formula $X\text{In}_2\text{Te}_4$ ($X = \text{Zn}, \text{Hg}$) have a body-centered tetragonal configuration with space group I-4 (#82). Each unit of $X\text{In}_2\text{Te}_4$ crystal contains two-X, four-In, and eight-Te atoms along with two vacancies per unit cell. Wyckoff atomic coordinates of $X\text{In}_2\text{Te}_4$ crystal are X (0, 0, 0), In^1 (0, 0, 0.5), In^2 (0, 0.5, 0.5) and Te (U_x, U_y, U_z), where U_x, U_y and U_z are anion displacement parameters in three axes. The value of lattice parameters has been calculated and listed in Table 1, which are in fair agreement with the available data reported experimentally and theoretically [31, 32]. The tetragonal distortion η ($= c/2a$) is 1 for the ideal structure, whereas the calculated values of η are 0.996 and 0.987 for ZnIn_2Te_4 and HgIn_2Te_4 , respectively, which equivalent to 1. This shows the presence of tetragonal distortion. The values

of anion displacement parameters (U_x , U_y , and U_z) and bond lengths (d_{X-Te} , d_{In^1-Te} and d_{In^2-Te}) for $ZnIn_2Te_4$ and $HgIn_2Te_4$ have been determined and presented in Table 1 along with the known values [8, 19, 33–35]. They agree well with the available reported values in the case of $ZnIn_2Te_4$. However, the values of these parameters for $HgIn_2Te_4$ are not available for comparison. Further, Table 1 shows that the bond lengths d_{In^1-Te} and d_{In^2-Te} are larger than d_{X-Te} . Figures 1(a) and 1(b) display the approximate band structures of $ZnIn_2Te_4$ and $HgIn_2Te_4$, respectively. This shows that both crystals are direct bandgap semiconductors with a bandgap of 1.398 eV and 1.101 eV along $\Gamma - \Gamma$ direction, respectively for $ZnIn_2Te_4$ and $HgIn_2Te_4$ at ambient conditions. The estimated bandgap E_g values are presented in Table 1, together with known data [7, 8, 19, 31–37]. The estimated values a , c , U_x , U_y , U_z , and E_g are also in fair concordance with the existing reported and experimental data.

Figs. 1 (a), 1 (b), and Fig. 1
Figs. 2 (a), 2 (b), and Fig. 2
Table 1

The density of states provides knowledge about a crystal's angular momentum character. The elements Zn, Hg, In, and Te have the electronic configurations $[Ar]3d^{10}4s^2$, $[Xe]4f^{14}5d^{10}6s^2$, $[Kr]4d^{10}5s^25p^1$ and $[Kr]4d^{10}5s^25p^4$, respectively. In the energy span of -15 eV to 10 eV, the total density of state (TDOS) and partial density of state (PDOS) have been computed and shown in Fig. 2. At 0 GPa pressure, Fig. 2 (a) shows the TDOS and PDOS for the Zn-4s/3p/3d, In-5s/5p, and Te-5s/5p states, which reveals that the valence band is divided into three parts. The first portion is mostly made up of Te-5s, with a small amount of In-5s and In-5p states. The second portion is strongly localized, owing to the presence of Zn-3d in -7.46 eV to -6.44 eV energy region. The valence band, which ranges from -6.09 eV to Fermi energy ($E_F = 0$ eV), is the third and final part. Mainly In-5s/5p and Te-5s/5p states give rise to make the third part. Figure 2 (a) reveals that the

valance band is primarily made up of Zn-4s, Te-5s, and Te-5p states, with In-5s and In-5p making a minor contribution. The major effect of In-5s/5p and Te-5s/5p, with an admixture of Zn-4s/3p/3d, forms the conduction band, which ranges from 1.90 eV to 6.91 eV. The TDOS and PDOS for Hg-6s/5p/5d, In-5s/5p and Te-5s/5p states has been shown in Fig. 2 (b). Figure 2 (b) shows that similar results have also been observed for HgIn_2Te_4 in the valence and conduction bands.

3.2. Elastic properties

Elastic parameters are essential parameters to convey the mechanical strength of any material. XIn_2Te_4 crystallizes in the tetragonal structure that comes under the Laue group T11 [4, 5]. Tetragonal Laue group T11 does not have an analytical formula to calculate elastic moduli as it contains off-diagonal shear elastic constant C_{16} . Due to this, seven elastic constants are obtained in the optimized structure. However, employing C_{16} equals zero, seven elastic constants of the Laue group T11 can be transformed into six elastic constants of the Laue group T1. Laue group T1 has a well-known formula to calculate the elastic constant from its six elastic stiffness constants C_{ij} , i.e., $C_{11}, C_{12}, C_{13}, C_{33}, C_{44}$ and C_{66} . Transformation of seven elastic stiffness coefficients of Laue group T11 into six elastic stiffness coefficients of Laue group T1 can be obtained through rotation around the z-axis with the angle given by following relations [4, 5]:

$$\phi_{\kappa, \gamma} = \frac{1}{4} \arctan \left(\frac{4C_{16}}{C_{11} - C_{12} - 2C_{66}} \right) \quad (1)$$

The above Eq. (1) gives the values of ϕ_{κ} and ϕ_{γ} within the range $0 < \phi < |\pi/2|$, where $\phi_{\gamma} = \phi_{\kappa} + \pi/4$. The value of ϕ_{κ} has been calculated using Eq. (1) and found to be 0.87° for ZnIn_2Te_4 and 2.30° for HgIn_2Te_4 at 0 GPa. Six independent elastic constants C_{ij} of Laue group T1

have been calculated using relations mentioned in Ref. [38, 39] by employing the LDA estimated seven elastic stiffness coefficients of Laue group T11 and angle ϕ_k . The values of these six coefficients, i.e., $C_{11}, C_{12}, C_{13}, C_{33}, C_{44}$ and C_{66} have been calculated at 0, 5, 10, 13, and 14 GPa pressures. For any stable tetragonal Laue group T1 crystal, all six independent elastic stiffness coefficients under pressure must fulfill the Born-Huang criteria as follows [40]:

$$C_{11} - P > 0; C_{44} - P > 0; C_{11} - C_{12} - 2P > 0; (C_{33} - P)(C_{11} + C_{12}) - 2(C_{13} - P)^2 > 0 \quad (2)$$

The estimated values of C_{ij} for ϕ_k at five different pressures are presented in Table 2 for XIn_2Te_4 . Plots have also been drawn between C_{ij} and pressure, and presented in Figs. 3 (a) and 3 (b), respectively, for ZnIn_2Te_4 and HgIn_2Te_4 . Figure 3 shows that the values of C_{ij} increase with the increasing pressure for both the materials. At 14 GPa, the value of C_{ij} defies the stability criteria mentioned above of Eq. (2) and turns into an unstable form, which indicates that XIn_2Te_4 is stable up to 13 GPa only. It has also been observed that the values of C_{11} and C_{33} are significantly higher than the values of C_{12}, C_{13}, C_{44} and C_{66} . This shows that the compounds are anisotropic and have more chances of shear deformation in the direction of a- and c- axes than compression deformation.

Figs. 3 (a), 3 (b), and Fig. 3
Figs. 4 (a), 4 (b), and Fig. 4
Table 2

Further, the value of elastic moduli of ZnIn_2Te_4 and HgIn_2Te_4 , such as shear modulus (G), bulk modulus (B), Poisson's ratio (ν), B/G , and Young's modulus (E) have been calculated at 0, 5, 10, 13, and 14 GPa using the relations given in Ref. [41]. The estimated values of these elastic moduli are presented in Table 2. The bulk modulus for ZnIn_2Te_4 and HgIn_2Te_4 is

35.322 GPa and 33.742 GPa, respectively, based on the extended Cohen formula given in Ref. [3]. The calculated values of bulk modulus B are in good agreement at 0 GPa. Elastic moduli (B , G and E) versus pressure plots are shown in Fig. 4 (a) and 4 (b) for ZnIn_2Te_4 and HgIn_2Te_4 respectively, which indicates that B , G and E increase with the increase of pressure. Frantsevich et al. [22, 42, 43] have proposed the critical limits of $\nu < 0.33$ and $B/G < 2.67$ for covalent (brittle) materials else it is ionic (ductile). The calculated values of ν and B/G indicate that both the semiconductors are of covalent behavior at 0 GPa. However, violate the inequalities and show the ionic (ductile) behavior at 5, 10, 13, and 14 GPa pressures. The Zener shear anisotropy factor's value (A) has been evaluated using the formula $A = 2C_{66} / (C_{11} - C_{12})$ [44] and presented in Table 2. For an anisotropic material, the value should be $A \neq 1$ otherwise material said to be isotropic material. Our calculated values of A also show the anisotropic character of both compounds.

Debye temperature (θ_D) is a constant that signifies the temperature of the highest form of a crystal's vibration, which is closely related to the specific heat and melting point of the compounds. Using data of G and B , Debye temperature values (θ_D) have been estimated based on relations given in Ref. [32, 45]. The calculated values of θ_D for ZnIn_2Te_4 and HgIn_2Te_4 have been presented in Table 2, together with the reported data [8]. The calculated value of θ_D for ZnIn_2Te_4 is found to be in fair agreement with reported values at 0 GPa [8]. However, the known values of θ_D for CdIn_2Te_4 and at other pressure are not available for comparison.

3.3. Optical properties

The frequency dependence complex dielectric function $\varepsilon(\omega) = \{\varepsilon_1(\omega) + i\varepsilon_2(\omega)\}$ is a prominent part of optical properties, which derives all other optical parameters such as extinction

coefficient $\alpha(\omega)$, reflectivity $R(\omega)$, refractive index $n(\omega)$, and energy loss function $L(\omega)$ using the relations mentioned in the literature [46–49]. The imaginary part $\varepsilon_2(\omega)$ of the complex dielectric function deals with the absorption of the incident photon, and the real part $\varepsilon_1(\omega)$ of the complex dielectric function concerns with the incident photons dispersion. The optical parameters such as the imaginary part $\varepsilon_2(\omega)$ and real part $\varepsilon_1(\omega)$ of complex dielectric function $\varepsilon(\omega)$ for XIn_2Te_4 have been estimated at 0, 5, 10, and 13 GPa pressures. Curves have also been plotted for $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ parameters in the energy range of 0 – 15 eV and presented in Figs. 5 and 6, respectively, for ZnIn_2Te_4 and HgIn_2Te_4 . The peak values of $\varepsilon_2(\omega)$ and $\varepsilon_1(\omega)$ parameters in Figs. 5 and 6 are marked as 'X,' which shows that in most cases, the peaks move in the direction of the high energy zone (blue-shift) with a change of pressure from 0 GPa to 5 GPa, 5 GPa to 10 GPa, and 10 GPa to 13 GPa. Further, the static dielectric constant $\varepsilon(0)$ has been calculated and presented in the last row of Table 2. A fair agreement has been found between them at 0 GPa [50]; however, they await experimental verification at other pressures.

Figs. 5 (a), 5 (b), and Fig. 5

Figs. 6 (a), 6 (b), and Fig. 6

4. Conclusions

The first-principle study is executed effectively to calculate the electronic, elastic, and optical properties for defect-chalcopyrite ZnIn_2Te_4 and HgIn_2Te_4 semiconductors at 0, 5, 10, 13, and 14 GPa pressures. The estimated values of electronic parameters such as lattice parameter (a and c), energy bandgap (E_g), anion displacement parameter (U_x , U_y , and U_z), and bond lengths ($d_{\text{X-Te}}$, $d_{\text{In}^1-\text{Te}}$ and $d_{\text{In}^2-\text{Te}}$) are presented in Table 1, which agree well with available reported and experimental values. The band structure shows that both compounds are indirect semiconductors

with an energy gap of 1.398 eV and 1.101 eV, respectively, for ZnIn_2Te_4 and HgIn_2Te_4 . The TDOS and PDOS plots of $\text{ZnIn}_2\text{Te}_4/\text{HgIn}_2\text{Te}_4$ demonstrate that Zn/Hg has a marginal effect around the Fermi level. However, the Te-5s/5p and In-5s/5p states dominate in the forming of valance and conduction bands. The value of $C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, C_{66}, G, B, E, A, \nu, B/G$ and θ_D have been estimated at 0, 5, 10, 13, and 14 GPa pressures and summarized in Table 2. The values of C_{ij} indicate that ZnIn_2Te_4 and HgIn_2Te_4 are stable up to 13 GPa and later becomes unstable. The calculated values of ν and B/G for ZnIn_2Te_4 and HgIn_2Te_4 are smaller than the critical limits of 0.33 and 2.67 at 0 GPa, which demonstrate the covalent behavior. Moreover, the estimated data of ν and B/G do not satisfy the criterion of critical limits at 5, 10, and 13 GPa, and hence show the presence of ionic behavior. The estimated values of static dielectric constant $\varepsilon(0)$ are listed in Table 2 at 0, 5, 10, and 13 GPa pressures, which indicates that the values of $\varepsilon(0)$ increase with the increasing pressure. The calculated static dielectric constant data under three different pressures of 5, 10, and 13 GPa are not available for comparison, as well as 12 elastic parameters and Debye temperature under four different pressures of 5, 10, 13, and 14 GPa are stated for the first time which await for experimental verification. The predicted values are generally in strong alignment with experimental and previously reported values, demonstrating the importance of this computational work. The values of these parameters are critical for future technological applications, such as selecting substrate materials and designing integrated circuits (ICs) for electro-optic systems. The predictive description of the computational methodology introduced in the present work is of immense significance and will mentor the forthcoming studies of these properties of new defect-chalcopyrite materials belong to the $\text{A}^{\text{II}}\text{B}_2\text{C}_4^{\text{VI}}$ family.

Acknowledgment

We express our sincere thanks to Prof. J. P. Pandey, Vice-Chancellor, M. M. M. University of Technology, Gorakhpur, for his continuous encouragement and motivation in conducting this work. The authors also thank Dr. Dharmendra Kumar and Dr. B. P. Pandey, M. M. M. University of Technology, Gorakhpur, for the valuable discussion for the presented results.

Conflict of interest The authors declare no conflicts of interest.

References

1. Kumar, P., Soni, A., Bhamu, K.C., Sahariya, J.: Optoelectronic behavioral study of defect-chalcopyrite semiconductors XGa_2Te_4 ($\text{X} = \text{Zn}, \text{Cd}$). *Materials Research Bulletin*. 86, 131–138 (2017). <https://doi.org/10.1016/j.materresbull.2016.10.012>
2. Zhang, S., Shi, L.: Structural, electronic, elastic and lattice dynamical properties of CdIn_2Te_4 under pressure from first principle. *International Journal of Modern Physics B*. 31, 1850026 (2017). <https://doi.org/10.1142/S0217979218500261>
3. Mishra, S., Ganguli, B.: Electronic and optical properties of defect CdIn_2Te_4 chalcopyrite semiconductor: A first principle approach. *Materials Chemistry and Physics*. 173, 429–437 (2016). <https://doi.org/10.1016/j.matchemphys.2016.02.034>
4. Gomis, O., Vilaplana, R., Manjón, F.J., Santamaría-Pérez, D., Errandonea, D., Pérez-González, E., López-Solano, J., Rodríguez-Hernández, P., Muñoz, A., Tiginyanu, I.M., Ursaki, V. V.: High-pressure study of the structural and elastic properties of defect-chalcopyrite HgGa_2Se_4 . *Journal of Applied Physics*. 113, 0–10 (2013). <https://doi.org/10.1063/1.4792495>
5. Gomis, O., Santamaría-Pérez, D., Vilaplana, R., Luna, R., Sans, J.A., Manjón, F.J., Errandonea, D., Pérez-González, E., Rodríguez-Hernández, P., Muñoz, A., Tiginyanu, I.M., Ursaki, V.V.: Structural and elastic properties of defect chalcopyrite HgGa_2S_4 under high pressure. *Journal of Alloys and Compounds*. 583, 70–78 (2014). <https://doi.org/10.1016/j.jallcom.2013.08.123>
6. Ouahrani, T., Reshak, A.H., Khenata, R., Amrani, B., Mebrouki, M., Otero-de-la-Roza, A., Luaña, V.: Ab-initio study of the structural, linear and nonlinear optical properties of CdAl_2Se_4 defect-chalcopyrite. *Journal of Solid State Chemistry*. 183, 46–51 (2010). <https://doi.org/10.1016/j.jssc.2009.09.034>

7. Jiang, X., Lambrecht, W.R.L.: Electronic band structure of ordered vacancy defect chalcopyrite compounds with formula II-III₂-VI₄. *Physical Review B*. 69, 035201 (2004). <https://doi.org/10.1103/PhysRevB.69.035201>
8. Ganguli, B., Krishna Saha, K., Saha-Dasgupta, T., Mookerjee, A., Bhattacharya, A.K.: Electronic and optical properties of ZnIn₂Te₄. *Physica B: Condensed Matter*. 348, 382–390 (2004). <https://doi.org/10.1016/j.physb.2004.01.004>
9. Bernard, J.E., Zunger, A.: Ordered-vacancy-compound semiconductors: Pseudocubic CdIn₂Se₄. *Physical Review B*. 37, 6835–6856 (1988). <https://doi.org/10.1103/PhysRevB.37.6835>
10. Errandonea, D., Kumar, R.S., Gomis, O., Manjón, F.J., Ursaki, V. V., Tiginyanu, I.M.: X-ray diffraction study on pressure-induced phase transformations and the equation of state of ZnGa₂Te₄. *Journal of Applied Physics*. 114, (2013). <https://doi.org/10.1063/1.4851735>
11. Errandonea, D., Kumar, R.S., Manjón, F.J., Ursaki, V. V., Tiginyanu, I.M.: High-pressure x-ray diffraction study on the structure and phase transitions of the defect-stannite ZnGa₂Se₄ and defect-chalcopyrite CdGa₂S₄. *Journal of Applied Physics*. 104, 063524 (2008). <https://doi.org/10.1063/1.2981089>
12. Gutiérrez, P.A., Sanjuán, M.L.: Ordinary and extraordinary phonons and photons: Raman study of anisotropy effects in the polar modes of MnGa₂Se₄. *Physical Review B*. 78, 045212 (2008). <https://doi.org/10.1103/PhysRevB.78.045212>
13. You, S.H., Hong, K.J., Jeong, T.S., Youn, C.J., Park, J.S., Shin, D.C., Moon, J.D.: Band gap energy and valence band splitting of p-CdIn₂Te₄ crystal by photocurrent spectroscopy. *Journal of Applied Physics*. 95, 4042–4045 (2004). <https://doi.org/10.1063/1.1686901>
14. Jeong, T.S., Hong, K.J.: Temperature dependence of intensity and peak position from photocurrent response in p-CdIn₂Te₄ crystal. *Journal of Applied Physics*. 96, 204–207 (2004). <https://doi.org/10.1063/1.1758311>
15. Misaki, T., Wakahara, A., Okada, H., Yoshida, A.: Epitaxial growth and characterization of ZnGeN₂ by metalorganic vapor phase epitaxy. *Journal of Crystal Growth*. 260, 125–129 (2004). <https://doi.org/10.1016/j.jcrysgro.2003.08.011>
16. Eifler, A., Riede, V., Hecht, J.-D., Krauss, G., Krämer, V., Grill, W.: On the Optical Properties of Defect-Chalcopyrite Single Crystals: The Aluminium Compounds HgAl₂Se₄, CdAl₂Se₄ and ZnAl₂Se₄. *Japanese Journal of Applied Physics*. 39, 98 (2000). <https://doi.org/10.7567/JJAPS.39S1.98>
17. Razzetti, C., Lottici, P.P.: Raman Scattering in Defective AIIIB₂III₄VI Compounds and Alloys. *Japanese Journal of Applied Physics*. 32, 431 (1993). <https://doi.org/10.7567/JJAPS.32S3.431>

18. Mayengbam, R., Tripathy, S.K., Palai, G., Dhar, S.S.: First-principles study of phase transition, electronic, elastic and optical properties of defect chalcopyrite ZnGa₂Te₄ semiconductor under different pressures. *Journal of Physics and Chemistry of Solids*. 119, 193–201 (2018). <https://doi.org/10.1016/j.jpcs.2018.03.027>
19. Ayeb, Y., Ouahrani, T., Khenata, R., Reshak, A.H., Rached, D., Bouhemadou, A., Arrar, R.: FP-LAPW investigation of structural, electronic, linear and nonlinear optical properties of ZnIn₂Te₄ defect-chalcopyrite. *Computational Materials Science*. 50, 651–655 (2010). <https://doi.org/10.1016/j.commatsci.2010.09.030>
20. Fuentes-Cabrera, M., Dong, J., Sankey, O.F.: Theoretical study of the structural, electronic and vibrational properties of CdIn₂Te₄. *Thin Solid Films*. 373, 19–22 (2000). [https://doi.org/10.1016/S0040-6090\(00\)01082-8](https://doi.org/10.1016/S0040-6090(00)01082-8)
21. Chandra, S., Kumar, V.: Structural, electronic and elastic properties of ZnGeN₂ and WZ-GaN under different hydrostatic pressures: A first-principle study. *International Journal of Modern Physics B*. 33, 1950297 (2019). <https://doi.org/10.1142/S0217979219502977>
22. Kumar, V., Chandra, S., Santosh, R.: First-Principles Calculations of the Structural, Electronic, Elastic and Optical Properties of LiGaS₂ and LiGaSe₂ Semiconductors Under Different Pressures. *Journal of Electronic Materials*. 47, 1223–1231 (2018). <https://doi.org/10.1007/s11664-017-5894-x>
23. Kumar, V., Singh, B.P., Pandey, B.P.: First-principle calculations of the elastic properties of semiconductors. *Computational Materials Science*. 87, 227–231 (2014). <https://doi.org/10.1016/j.commatsci.2014.02.010>
24. Srivastava, V.K.: Ionicity in AlIBIVCV₂. *Physical Review B*. 36, 5044–5046 (1987). <https://doi.org/10.1103/PhysRevB.36.5044>
25. Kumar, V., Chandra, S.: Second-Order Nonlinear Optical Tensor Coefficients of LiXTe₂ (X = Al, Ga, In) Chalcopyrite Semiconductors. *Crystal Research and Technology*. 53, 1800133 (2018). <https://doi.org/10.1002/crat.201800133>
26. Segall, M.D., Lindan, P.J.D., Probert, M.J., Pickard, C.J., Hasnip, P.J., Clark, S.J., Payne, M.C.: First-principles simulation: Ideas, illustrations and the CASTEP code. *Journal of Physics Condensed Matter*. 14, 2717–2744 (2002). <https://doi.org/10.1088/0953-8984/14/11/301>
27. Ceperley, D.M., Alder, B.J.: Ground state of the electron gas by a stochastic method. *Physical Review Letters*. 45, 566–569 (1980). <https://doi.org/10.1103/PhysRevLett.45.566>
28. Perdew, J.P., Zunger, A.: Self-interaction correction to density-functional approximations for many-electron systems. *Physical Review B*. 23, 5048–5079 (1981). <https://doi.org/10.1103/PhysRevB.23.5048>
29. Hamann, D.R., Schlüter, M., Chiang, C.: Norm-Conserving Pseudopotentials. *Physical Review Letters*. 43, 1494–1497 (1979). <https://doi.org/10.1103/PhysRevLett.43.1494>

30. Fischer, T.H., Almlöf, J.: General methods for geometry and wave function optimization. *Journal of Physical Chemistry*. 96, 9768–9774 (1992). <https://doi.org/10.1021/j100203a036>
31. Hahn, H., Frank, G., Klingler, W., Störger, A.D., Störger, G.: Untersuchungen über ternäre Chalkogenide. VI. Über Ternäre Chalkogenide des Aluminiums, Galliums und Indiums mit Zink, Cadmium und Quecksilber. *Zeitschrift für anorganische und allgemeine Chemie*. 279, 241–270 (1955). <https://doi.org/10.1002/zaac.19552790502>
32. Haynes, W.M., Lide, D.R., Bruno, T.J.: *CRC Handbook of Chemistry and Physics*, 97th Edition. (2017)
33. Suriwong, T., Kurosaki, K., Thongtem, S., Harnwungmoung, A., Plirdpring, T., Sugahara, T., Ohishi, Y., Muta, H., Yamanaka, S.: Synthesis and thermal conductivities of ZnIn_2Te_4 and CdIn_2Te_4 with defect-chalcopyrite structure. *Journal of Alloys and Compounds*. 509, 7484–7487 (2011). <https://doi.org/10.1016/j.jallcom.2011.04.086>
34. Garbato, L., Ledda, F., Rucci, A.: Structural distortions and polymorphic behaviour in ABC_2 and AB_2C_4 tetrahedral compounds. *Progress in Crystal Growth and Characterization*. 15, 1–41 (1987). [https://doi.org/10.1016/0146-3535\(87\)90008-6](https://doi.org/10.1016/0146-3535(87)90008-6)
35. Reguieg, S., Baghdad, R., Abdiche, A., Bezzerrouk, M.A., Benyoucef, B., Khenata, R., Bin-Omran, S.: First-Principles Study of Structural, Optical, and Thermodynamic Properties of ZnIn_2X_4 ($\text{X} = \text{Se}, \text{Te}$) Compounds with DC or DF Structure. *Journal of Electronic Materials*. 46, 401–412 (2017). <https://doi.org/10.1007/s11664-016-4831-8>
36. MacKinnon: Numerical Data and Functional Relationships in Science and Technology. In: *Table of Numerical Data and Functional Relationships in Science and Technology*. p. 124. Springer-Verlag, Berlin (1985)
37. Manca, P., Raga, F., Spiga, A.: Photoconductivity of ZnIn_2Se_4 and ZnIn_2Te_4 . *Physica Status Solidi (a)*. 16, K105–K108 (1973). <https://doi.org/10.1002/pssa.2210160243>
38. Farley, J.M., Saunders, G.A.: Ultrasonic study of the elastic behaviour of calcium tungstate between 1.5 K and 300 K. *Journal of Physics C: Solid State Physics*. 5, 3021–3037 (1972). <https://doi.org/10.1088/0022-3719/5/21/008>
39. Farley, J.M., Saunders, G.A., Chung, D.Y.: The elastic constants of strontium molybdate (ultrasound velocity data). *Journal of Physics C: Solid State Physics*. 6, 2010–2019 (1973). <https://doi.org/10.1088/0022-3719/6/12/004>
40. Mouhat, F., Coudert, F.X.: Necessary and sufficient elastic stability conditions in various crystal systems. *Physical Review B - Condensed Matter and Materials Physics*. 90, 0–3 (2014). <https://doi.org/10.1103/PhysRevB.90.224104>
41. Caracas, R., Boffa Ballaran, T.: Elasticity of $(\text{K}, \text{Na})\text{AlSi}_3\text{O}_8$ hollandite from lattice dynamics calculations. *Physics of the Earth and Planetary Interiors*. 181, 21–26 (2010). <https://doi.org/10.1016/j.pepi.2010.04.004>

42. Frantsevich, I.N., Voronov, F.F., Bokuta, S.A.: Elastic Constants and Elastic Moduli of Metals and Insulators. , Naukova Dumka, Kiev (1982)
43. Vaitheeswaran, G., Kanchana, V., Kumar, R.S., Cornelius, A.L., Nicol, M.F., Svane, A., Delin, A., Johansson, B.: High-pressure structural, elastic, and electronic properties of the scintillator host material KMgF₃. *Physical Review B*. 76, 014107 (2007).
<https://doi.org/10.1103/PhysRevB.76.014107>
44. Ouahrani, T., Reshak, A.H., Khenata, R., Amrani, B., Mebrouki, M., Otero-de-la-Roza, A., Luaña, V.: Ab-initio study of the structural, linear and nonlinear optical properties of CdAl₂Se₄defect-chalcopyrite. *Journal of Solid State Chemistry*. 183, 46–51 (2010).
<https://doi.org/10.1016/j.jssc.2009.09.034>
45. Anderson, O.L.: A simplified method for calculating the debye temperature from elastic constants. *Journal of Physics and Chemistry of Solids*. 24, 909–917 (1963).
[https://doi.org/10.1016/0022-3697\(63\)90067-2](https://doi.org/10.1016/0022-3697(63)90067-2)
46. Tributsch, H.: Solar Energy-Assisted Electrochemical Splitting of Water. Some Energetical, Kinetical and Catalytical Considerations Verified on MoS₂ Layer Crystal Surfaces. *Zeitschrift für Naturforschung A*. 32, (1977). <https://doi.org/10.1515/zna-1977-0911>
47. Wooten, F.: Optical Properties Of Solids. Academic Press. 260 (1972).
[https://doi.org/10.1016/0165-1633\(89\)90057-9](https://doi.org/10.1016/0165-1633(89)90057-9)
48. Dadsetani, M., Pourghazi, A.: Optical properties of strontium monochalcogenides from first principles. *Physical Review B - Condensed Matter and Materials Physics*. 73, 1–7 (2006). <https://doi.org/10.1103/PhysRevB.73.195102>
49. Sahin, S., Ciftci, Y.O., Colakoglu, K., Korozlu, N.: First principles studies of elastic, electronic and optical properties of chalcopyrite semiconductor ZnSnP₂. *Journal of Alloys and Compounds*. 529, 1–7 (2012). <https://doi.org/10.1016/j.jallcom.2012.03.046>
50. Neumann, H., Kissinger, W., Lévy, F.: High-frequency dielectric constant of AIIB₂IIIC₄VI ordered-vacancy compounds. *Crystal Research and Technology*. 25, 1189–1193 (1990). <https://doi.org/10.1002/crat.2170251015>

Table 1. Optimized values of lattice parameters (a=b and c), unit cell volume (V_0), internal parameters (U_x , U_y and U_z), bond lengths (d_{X-Te} , d_{In^1-Te} and d_{In^2-Te}), and energy bandgap (E_g) for $ZnIn_2Te_4$ and $HgIn_2Te_4$ defect-chalcopyrite semiconductors.

Compounds.		a (Å)	c (Å)	V_0 (Å ³)	U_x	U_y	U_z	d_{X-Te} (Å)	d_{In^1-Te} (Å)	d_{In^2-Te} (Å)	E_g (eV)
$ZnIn_2Te_4$	This work	6.045	12.044	434.517	0.270	0.218	0.137	2.655	2.734	2.726	1.398
	Expt.	6.11 ^a , 6.132 ^b	12.2 ^a , 12.292 ^b		0.26 ^b	0.24 ^b	0.13 ^b				1.87–1.90 ^c
	Rep.	6.122 ^d , 6.494 ^e , 6.12 ^f , 6.11 ^g	12.24 ^d , 12.887 ^e , 12.24 ^f , 12.22 ^g		0.2485 ^e , 0.261 ^f , 0.25 ^g , 0.269 ^h	0.250 ^e , 0.221 ^f , 0.25 ^g , 0.208 ^h	0.1256 ^e , 0.130 ^f , 0.125 ^g , 134 ^h				1.90 ⁱ , 1.4 ^j
$HgIn_2Te_4$	This work	6.125	12.084	446.833	0.277	0.225	0.141	2.757	2.736	2.726	1.101
	Expt.	6.17 ^a	12.3 ^a								
	Rep.	6.186 ^d	12.37 ^d								1.37 ⁱ

^a Reference [31], ^b Reference [33], ^c Reference [36], ^d Reference [32], ^e Reference [19], ^f Reference [34], ^g Reference [8], ^h Reference [35], ⁱ Reference [7],

^j Reference [37]

Table 2. Calculated values of elastic constants C_{ij} in GPa, bulk modulus B in GPa, Shear modulus G in GPa, Young's modulus E in GPa, Poisson's ratio ν , B/G ratio, Zener anisotropy factor A and Debye temperature θ_D in °K under different pressure for $ZnIn_2Te_4$ and $HgIn_2Te_4$.

Elastic parameters	$ZnIn_2Te_4$						$HgIn_2Te_4$					
	At 0 GPa		This work at				At 0 GPa		This work at			
	This work	Rep.	5 GPa	10 GPa	13 GPa	14 GPa	This work	Rep.	5 GPa	10 GPa	13 GPa	14 GPa
C_{11}	71.59		101.15	129.06	125.87	138.56	61.27		90.39	116.08	127.40	125.80
C_{33}	52.53		81.88	95.77	107.90	109.51	53.19		79.56	101.32	109.75	115.63
C_{44}	28.91		36.00	39.14	30.35	22.46	24.32		35.71	38.78	20.53	26.08
C_{66}	13.74		20.63	19.79	38.35	24.08	13.06		27.62	32.00	26.89	30.44
C_{12}	23.60		49.05	65.69	94.78	88.69	19.90		58.59	85.76	87.94	95.02
C_{13}	29.93		52.34	74.22	85.67	90.80	27.62		56.01	79.17	88.92	95.01
B	39.27	35.322 [*]	64.44	85.21	97.27	101.28	35.61	33.742 [*]	65.71	89.64	98.33	103.34
G	20.79		26.40	27.15	24.60	21.24	18.48		24.18	25.73	19.89	20.88
E	53.02		69.69	73.64	68.07	59.57	47.26		64.61	70.45	55.91	58.69
ν	0.27		0.32	0.36	0.38	0.40	0.28		0.34	0.37	0.41	0.41
B/G	1.89		2.44	3.14	3.95	4.77	1.93		2.72	3.48	4.94	4.95
A	0.50		0.67	0.55	1.93	0.85	0.56		1.39	1.60	1.14	1.66
θ_D	195.376	175 ^g , §	221.411	225.617	215.569	200.824	172.736		199.037	206.240	182.256	186.729
$\varepsilon(0)$	11.885	7.1±0.3 ^a	13.348	14.566	15.730		10.407	8.55 ^a	11.860	13.076	13.756	

^a Reference [50],

§ Experimental value,

* Value calculated based upon extended Cohen formula given in Ref. [3]

(a)

(b)

Fig. 1. Electronic band structure of (a) ZnIn_2Te_4 (1.398 eV) and (b) HgIn_2Te_4 (1.101 eV).

(a)

(b)

Fig. 2. DOS for (a) ZnIn_2Te_4 and (b) HgIn_2Te_4 .

Fig. 3. Elastic constants vs pressure curve for (a) ZnIn_2Te_4 and (b) HgIn_2Te_4 .

Fig. 4. (a) Elastic moduli vs pressure curve for (a) ZnIn_2Te_4 and (b) HgIn_2Te_4 .

Fig. 5. Optical properties of ZnIn₂Te₄: (a) real part dielectric function and (b) imaginary part of the dielectric function.

Fig. 6. Optical properties of HgIn₂Te₄: (a) real part dielectric function and (b) imaginary part of the dielectric function.