First Principle Study of Structural, Electronic, and Optical Properties of XIn$_2$S$_4$ (X = Zn, Cd, Hg)

Jameelah Alzahrani$^1$, Samah Al-Qaisi$^2$, Q. Mahmood$^{1*,}$, T. Ghrib$^1$

$^1$Department of physics, College of Science, Imam Abdulrahman Bin Faisal University, P.O. Box 1982, 31441, City Dammam, Saudi Arabia

$^2$Palestinian Ministry of Education and Higher Education, Nablus, Palestine

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ABSTRACT

The spinel oxides are one of the prime candidates for their use in thermoelectric and optoelectronic applications. This particular article mainly deals with the thermodynamic and mechanical stabilities of spinel sulfides confirmed by formation energy and Born-mechanical stability criteria. The ductile behavior is achieved through Poisson's and Pugh's ratios. The indirect band gaps of 1.9 eV, 1.7 eV and direct band gap of 1.3 eV for ZnIn$_2$S$_4$, CdIn$_2$S$_4$ and HgIn$_2$S$_4$ spinel sulfides, respectively, are estimated by employing modified Becke-Johnson (mBJ) potential in the Wien2k computational program. The calculated optical characteristics such as dielectric coefficient, refractive index, absorption, reflection, energy loss coefficient and other related parametric quantities are explored to observe optoelectronic applications from UV to visible energy range as we move from Zn to Hg. Moreover, the ratios of thermal conductivity to electrical conductivity, Seebeck coefficient along with the figure of merits (ZT) are discussed to acknowledge the thermoelectric behavior of all three materials. The high values of ZT 0.84/0.74/0.79 are observed for Zn/Cd/HgIn$_2$S$_4$ spinel sulfides which ensure their prospective use in thermal energy conversion devices, especially in thermoelectric generators.

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*Corresponding Author’s Email: gmmustafa@iau.edu.sa

1. Introduction

The chemical formula of Spinals is AB$_2$X$_4$ (where A and B are most likely divalent and trivalent metallic cations, respectively), and X is an anion that forms tetrahedrons and octahedrons around A and B ions, respectively (Bragg, 1915; Nishikawa, 1915). The large variety of verified synthesis techniques for the fabrication of spinels made it feasible to tune their surface features and lattice parameters (Cheng et al., 2011; Radaelli et al., 2002), consequently, fluctuating valence states of individual atoms and their relevant compositions have demonstrated robust impact upon physical characteristics of material (Cho, Lee, Lee, Hong, & Cho, 2011; Kaczmarczyk et al., 2016; Marco et al., 2001; Sonoyama, Kawamura, Yamada, & Kanno, 2006; Zhao, Yan, Chen, & Chen, 2017). In spite of the fact that transparent conducting materials (TCM) have been proved to be valuable for diverse commercial optical applications (Brunin, Ricci, Ha, Rignanese, & Hautier, 2019), but still, traditional transparent conducting oxides (TCOs) shows complex characteristics because of the microstructures’ complexity (Ginley & Bright, 2000). That's why a large part of material research community is still bus to find more efficient methods and advanced transparent conducting materials for their limitless applications in commercial optoelectronic devices. In recent years, Spinels AB$_2$X$_4$ have attracted many researchers to study the physical properties (Kefeni & Mamba, 2020; Narang & Pubby, 2021; Singh Yadav et al., 2020; Tsurkan, Krug von Nidda, Delsenhofer, Lunkenheimer, & Loidl, 2021).
A plethora of research reports is present related to the investigation of the physical properties of AB$_2$S$_4$. In 1969, ZnIn$_2$S$_4$ was synthesized by Range et al. The stability of cubic ZnIn$_2$S$_4$ spinel was ensured, even after a period of one year, no transformation from cubic to any other phase was admitted by ZnIn$_2$S$_4$ at room temperature and atmospheric pressure even after a period of one year (Sriram et al., 1998). The reflectivity spectra of AB$_2$S$_4$ (A=Zn, Cd and B=In, Ga) were studied for a wide energy range of 1-8 eV under the action of unpolarized light at room temperature (Turowski, Kisel, & Giriati, 1984). S. K. Batabyal et al. used the one-pot method to synthesize In$_2$S$_3$, ZnIn$_2$S$_4$, and CdIn$_2$S$_4$. Afterward, they used X-ray powder diffraction (XRPD), transmission and scanning electron microscopies (TEM & SEM), selected area electron diffraction (SAED) patterns, and energy-dispersive X-ray analysis (EDX) for the characterization purposes of nano-crystals (Batabyal, Lu, & Vittal, 2016). The effect of change in temperature on the electronic and optical properties of HgIn$_2$S$_4$, has been calculated for the temperature interval of 10-300 K (Syrbu, Tiron, & Zalamai, 2019). The ab-initio calculations of structural parameters, electronic properties, and transport properties were conducted by employing GGA along with SOC (spin-orbital coupling) for HgIn$_2$S$_4$ and ZnIn$_2$S$_4$ by using FP-LAPW+LO method (Kotbi, Hartiti, Fadili, Ridah, & Thevenin, 2019). The photoluminescence of MgIn$_2$S$_4$ and HgIn$_2$S$_4$ have revealed that donor-acceptor transmissions are dominant in the strong emission bands, which can also be observed in other members of this family (Fortin, Fafard, Annedda, Ledda, & Charlebois, 1991). The known physical characteristics highlighted that XIn$_2$S$_4$ (X=Zn, Cd, and Hg) can be used in various devices for commercial as well as domestic use such as; Light-emitting diodes (LED), solar cells, photocatalysis, photosensors, charge storage devices, thermoelectricity, photoconductors (Chen et al., 2016; Ling et al., 2017; Wang et al., 2021; Zhang et al., 2022).

Although, multiple reports are accessible related to the study of ZnIn$_2$S$_4$, CdIn$_2$S$_4$ and HgIn$_2$S$_4$ by varying X = Zn, Cd, Hg. But, as per our best knowledge, no comprehensive report is present related to the physical properties, especially the thermodynamic and detailed optical response of XIn$_2$S$_4$ (X = Zn, Cd, Hg). In this report, we present optoelectronic and thermoelectric properties of XIn$_2$S$_4$ (X = Zn, Cd, Hg) by using mBJ potential with the help of density functional theory-based calculations.

2. Method of Calculations

This work includes in-depth study of band structure, optical properties, and thermoelectric performances of XIn$_2$S$_4$ (X = Zn, Cd, Hg) spinel sulfides that have been studied by using Wien2k computational code (Peter Blaha, Schwarz, Madsen, Kvasnicka, & Luitz, 2001). In order to accurately calculate the Hamiltonian, Wien2k is built on FP-LAPW method (P Blaha & Schwarz, 1987) supported by various potentials and approximations. The Kohn-sham scheme along with PBE-GGA approximation was utilized to compute structural parameters of ground state, which was initially followed by the Murnaghan equation of state. Since PBE-GGA accurately estimates the ground-state parameters but underestimates electronic band structures. The electronic band structures are calculated by using mBJ potential (Koller, Tran, & Blaha, 2011; Tran & Blaha, 2009) to establish exact exchange and correlation with the help of following mathematical equation:

$$ v_{x,\sigma}^{mBJ}(r) = c v_{x,\sigma}^{BR}(r) + (3c - 2) \frac{1}{12} \frac{\sqrt{\frac{2}{\rho_i(r)}}}{\rho_i(r)} $$

(1)

Where $\rho_i(r)$ is density of states, $v_{x,\sigma}^{BR}(r)$ is Becke-Roussel (BR) potential, and c is charge convergence. The calculations for optical and thermoelectric characteristics of XIn$_2$S$_4$ (X = Zn, Cd, Hg) were followed by the electronic structures calculated with the help of mBJ potential. Kramer kroning relation (Wooten, 2013) is used to extract the optical properties in Wien2k code. While the thermoelectric properties are predicted by mean of transport coefficient in BoltzTraP code (Madsen & Singh, 2006; Scheidemantel, Ambrosch-Draxl, Thonhauser, Badding, & Sofo, 2003).

The transport distribution functions were used to obtain the Seebeck coefficient and thermoelectric conductivity as:

$$ \sigma_{\alpha\beta}(\alpha, \mu) = \frac{1}{N} \int \sigma_{\alpha\beta}(\epsilon) \left( -\frac{\partial f_i(T, \epsilon, \mu)}{\partial \epsilon} \right) d\epsilon $$

(2)
\[
S_{\alpha\beta}(T,\mu) = \frac{1}{\epsilon^2 n S_{\alpha\beta}(T,\mu)} \int \sigma_{\alpha\beta}(\epsilon - \mu)[-\frac{\partial f_0(T,\epsilon,\mu)}{\partial \epsilon}] d\epsilon
\]  

(3)

Where \( \mu \), \( \Omega \), and \( f_0 \) shows the chemical potential, unit cell volume, and Fermi-Dirac distribution function respectively. In terms of BoltzTraP code, the relaxation time is \( 10^{-14} \) s.

The rigid band approximation is used for evaluating the properties relative to the Fermi energy (Ryu & Oh, 2016). Moreover, the product of muffin-tin radius (\( R_{\text{MT}} \)) and reciprocal lattice wave vector is 8. The maximum angular momentum \( l_{\text{max}} \) is 10. \( G_{\text{max}} \) is set to 16 (Ry)^{1/2}. The K-point grid is set to 10x10x10 along with 1000 k-points, after analyzing various k-mesh orders. 35 Monk Horst-Pack k-points have been engaged for the charge/energy convergence test fixed at 0.00001 Ry, after which all three cases have shown constant energy that shows fully converged structure.

3. Results and Discussion

3.1. Thermodynamic and Mechanical Stability

Spinel sulfides \( \text{XIn}_2\text{S}_4 \) (\( \text{X} = \text{Zn}, \text{Cd}, \text{Hg} \)) are optimized in cubic phase by using PBE-GGA approximation and plotted in Fig.2. The atomic coordinates of \( \text{X} \), \( \text{In} \) and \( \text{S} \) are (1/8, 1/8, 1/8), (1/2, 1/2, 1/2) and (1/4, 1/4, 1/4) accompanied by 227-Fd3m space group. The inter-atomic strain forces are condensed up to 0.0001 GPa to achieve more stabilized structures. The lattice constants and bulk modulus are evaluated by applying Murnaghan equation of state, summarized in Table 1. Computed lattice parameters improve from \( \text{ZnIn}_2\text{S}_4 \) to \( \text{HgIn}_2\text{S}_4 \), as well as, decay in bulk modulus have been witnessed due to varying ionic size from \( \text{Zn} \) to \( \text{Hg} \). By using the following expression thermodynamic stability is ensured by analyzing enthalpy of formation (Mahmood et al., 2019):

\[
\Delta H_f = E_{\text{Total}}(\text{XIn}_2\text{S}_4) - lE_X - mE_{\text{In}} - nE_S
\]  

(4)

Here, \( E_{\text{Total}}(\text{XIn}_2\text{S}_4) \) expresses spinel’s total energy. The bulk form energies for \( \text{X} \) (\( \text{Zn}, \text{Cd}, \text{Hg} \)), \( \text{In} \) and \( \text{S} \) are denoted by \( E_X \), \( E_{\text{In}} \) and \( E_S \), respectively. In all three cases the value of enthalpy is negative which divulge thermodynamically stable of considered spinal sulfides in cubic phases. Noticeable improvements have been witnessed in the enthalpy of formation by replacement of \( \text{X} \)-cations from \( \text{Zn} \) to \( \text{Hg} \), which portray higher stability due to tetrahedral and octahedral positions that turn out to be welcoming to the cations.

Figure 1: Computed (a) Crystal Structure, (b) Bond lengths, and (c) Polyhedral of \( \text{XIn}_2\text{S}_4 \) (\( \text{X} = \text{Zn}, \text{Cd}, \text{Hg} \))
Figure 2: Optimized energy versus volume plots (a) ZnIn$_2$S$_4$, (b) CdIn$_2$S$_4$, and (c) HgIn$_2$S$_4$

### 3.2. Electronic Properties

In order to understand the electronic behavior of considered materials, the electronic band gap have been calculated by applying two well-known approximations (PBE-GGA functional and mBJ potential). The problem with PBE-GGA approximation is that it underestimates the electronic band structure which can be resolved by using mBJ potential which improves electronic band gap as compared to the computed band gap with the help of PBE-GGA. The indirect bandgap of 1.9eV, 1.7eV and direct bandgap of 1.3eV have been visualized for ZnIn$_2$S$_4$, CdIn$_2$S$_4$ and HgIn$_2$S$_4$, respectively as shown in Fig.3. The decrease in bandgap with the increase in atomic radii has been observed, which ensures that electronic band gap of spinel sulfides is tunable within ultraviolet and visible energy range, which further points out to the prospect of altering the optical characteristics for range of optoelectronic devices.

Figure 3: The band structures of (a) ZnIn$_2$S$_4$, (b) CdIn$_2$S$_4$, and (c) HgIn$_2$S$_4$
3.3. Optical Properties

Optical features are elaborated through interaction of light with matter, during which electrons absorb light and display inter- and intra-band electronic transitions. For optical applications purposes, the inter-band transitions are relatively more appropriate as compared to the intra-band transitions which occur within bands. Moreover, band gap of any compound has its own importance in optical behavior of any material due to the energy region having higher rate of absorption and exposure of the absorption edge (Fox, 2002; Khan, Kashyap, Solanki, Nautiyal, & Auluck, 1993; Ramay, Hassan, Mahmood, & Mahmood, 2017; Rashid et al., 2019; Zerarga, Bouhemadou, Khenata, & Bin-Omran, 2011). Several optical constraints calculated for all three materials are shown in Fig. 4(a-h). The complex dielectric constant $\varepsilon(\omega) = \operatorname{Re} \varepsilon(\omega) + \operatorname{Im} \varepsilon(\omega)$ is calculated to examine light polarization, absorption, and dispersion of incident light. The real part ($\operatorname{Re} \varepsilon(\omega)$) and imaginary ($\operatorname{Im} \varepsilon(\omega)$) parts are linked together via Kramer-Krong relation (Horsley, Artoni, & La Rocca, 2015):

$$
\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega',
$$

$$
\varepsilon_2(\omega) = \frac{e^2 n^2}{(\pi m^*)^2} \sum_{n'\ell} \int_0^\infty M_{n'\ell\ell}(k) [2\delta(\omega_{n'\ell\ell}(k) - \omega) - k] d^3k
$$

Here $P$ is the principal integral. The plots for $\operatorname{Re} \varepsilon(\omega)$ are given in Fig. 4a. The static value of $\operatorname{Re} \varepsilon(\omega)$ and calculated band gaps are in agreement with the Penn’s model; $\operatorname{Re} \varepsilon(0) \approx 1 + (h\omega_p/E_0)^2$, where $h$ is the Planck constant and $\omega_p$ is the frequency of incident photons (Penn, 1962; Yazdanbakhsh, Khosravi, Goharshadi, & Youssefi, 2010). The maximum values of $\operatorname{Re} \varepsilon(\omega)$ are achieved at 4.0 eV, 3.8 eV and 3.6 eV, which have shown huge variation with more increase in energy. The small humps in the energy range 5-6 eV are result of electronic transitions from occupied to unoccupied states. These values agree with stated band structures displayed in Fig. 3.

The imaginary dielectric coefficient is shown in Fig. 4b which describes the optical absorption of the considered materials. The absorption edge after which the absorption of incident photons starts to increase can be approximated with the help of the band gap. The energy of absorption edge for examined $\operatorname{Im} \varepsilon(\omega)$ graph agrees with relevant band gap as shown in Fig. 3. The intense peaks appeared at 4.3 eV, 4.1 eV, and 3.9 eV, for ZnIn$_2$S$_4$, CdIn$_2$S$_4$, and HgIn$_2$S$_4$, respectively. Therefore, maximum absorption is witnessed in UV region, that ensures their possible applicability in sterilization of surgical equipment and optoelectronics devices especially made to be used in ultraviolet region.

The refractive index $n(\omega)$, extinction coefficient $k(\omega)$ and $\operatorname{Re} \varepsilon(\omega)$ are interrelated with each other, as stated in the equation: $n^2 - k^2 = \operatorname{Re} \varepsilon(\omega)$. The dimensionless $n(\omega)$ determine variation in the speed of light in particular material as compared to speed of light in the air and spreads wavelengths of incident light into its constituent colors, like $\operatorname{Re} \varepsilon(\omega)$. The refractive index of transparent medium is somewhere in between 1 to 3 for visible light. Thus, the refractive indexes of these three spinels are suitable for numerous optoelectronic applications. The sharp peaks of refractive indices appear at 4.0 eV, 3.8 eV, and 3.6 eV, for ZnIn$_2$S$_4$, CdIn$_2$S$_4$, and HgIn$_2$S$_4$, respectively, as displayed in Fig. 4c. The displayed refractive index $n(0)$ at zero frequency and $\operatorname{Re} \varepsilon(0)$ at zero frequency agrees according to the equation stated earlier, which verifies the accuracy of the computed results. The extinction coefficient and refractive index are related to the imaginary part of the dielectric coefficient by the expression; $2nk(\omega) = \operatorname{Im} \varepsilon(0)$ and demonstrate similarity in the behavior of extinction coefficient and $\operatorname{Im} \varepsilon(\omega)$, as illustrated in Fig. 4d.

The absorption coefficient is calculated to visualize the absorptive nature of considered materials under the influence of incident photons passing through the particular materials is plotted in Fig. 4e. From energy value 0 eV to 1.9 eV, 1.7 eV, and 1.3 eV, for ZnIn$_2$S$_4$, CdIn$_2$S$_4$, and HgIn$_2$S$_4$, respectively, negligible absorption can be seen from Fig. 4e, which signify the threshold limit and is comparable to the band gaps observed from the measured band structures. The intensified rate of absorption of light occurs in UV-region as manifested earlier from $\operatorname{Im} \varepsilon(\omega)$ and $k(\omega)$.
Figure 4: Computed (a) $\varepsilon_1(\omega)$, (b) $\varepsilon_2(\omega)$, (c) $n(\omega)$, (d) $k(\omega)$, (e) $\alpha(\omega)$, (f) $\sigma(\omega)$, (g) $R(\omega)$, and (h) $L(\omega)$ for XIn$_2$S$_4$ (X = Zn, Cd, and Hg) where lines of Black, Red and Green color plots the information of ZnIn$_2$S$_4$, CdIn$_2$S$_4$ and HgIn$_2$S$_4$, respectively.

Under the influence of light, the electrons in the valence band jumps to conduction band and generates photocurrent after sufficient energy which is required to cross the band gap energy, for that reason, optical conductivity $\sigma(\omega)$ of material increases with increase in the energy of incident light after the defined band gap. The computed $\sigma(\omega)$ are plotted in Fig. 4f, which confirms the parallel trends as seen from the absorption coefficient. The irregular behavior of the calculated reflectivity $R(\omega)$ for XIn$_2$S$_4$ (X = Zn, Cd, and Hg) is exposed in Fig. 4g. It shows high value but less than 0.4 in the energy range 3.5 eV to 4.5 eV. The energy loss $L(\omega)$ is illustrated in Fig. 4h, from which it is crystal clear that the energy loss in the visible region is very small, leading to the fact that these materials can be used for potential uses in optical device fabrication applicable in visible energy region.
4. **Conclusion**

This manuscript contains the detailed information about electronic, optical and thermodynamic behavior of cubic ZnIn$_2$S$_4$, CdIn$_2$S$_4$, and HgIn$_2$S$_4$ spinel sulfides. The negative enthalpy of formation guarantees the thermodynamic stability. The band gap is tuned from ultraviolet to visible energies by replacing Zn to Cd and Hg. ZnIn$_2$S$_4$ have shown maximum absorption in UV region. The overall absorption for CdIn$_2$S$_4$ in low energy reveals that it is a worthy choice for optoelectronic device fabrication for visible region. Furthermore, the band gap (1.3 eV) of HgIn$_2$S$_4$ is considered most suitable for optoelectronics. The optical loss and reflectivity are negligible in the visible region of spectrum which is ideal for optical applications.

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