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DENSITY FUNCTIONAL THEORY STUDIES OF ELECTRONIC AND THERMAL PROPERTIES OF ZNSIP SEMICONDUCTOR

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Abstract- First principles calculation within density functional theory (DFT) has been used to calculate the electronic, optical and thermal properties of $ZnSiP_2$ chalcopyrite semiconductor. The result of band structure, total density of state (DOS) and partial density of state (PDOS) have been discussed. The dielectric constant, refractive index, reflectivity, absorption coefficients, extinction coefficient and loss function have been presented in energy range of 0-25 eV. The values of melting point, Debye temperature, heat of formation and bulk modulus have been calculated. The calculated values of these parameters are in good agreement with the experimental values and the value reported by previous researchers.

Keywords- *DFT; Electronic structure; Optical properties; Thermal properties*

I. INTRODUCTION

During last few decades considerable amount of experimental and theoretical work has been done to understand the various electronic and thermal properties of I-III-VI_2 and II-IV-V_2 groups of chalcopyrite semiconductors because of their wide applications in the fields of linear and nonlinear optical devices [1]. Several workers have used different techniques such as density functional theory (DFT) [2-7], full potential linear augmented plane wave plus local orbit method (FP-LAPW+lo) [8-9] and X-ray diffraction [10] to investigate the electronic, optical and thermal properties of these chalcopyrites. Kumar et al. [11-13] have explained these properties using plasma oscillation theory of solids. Among these large families of chalcopyrites, $ZnSiP_2$ is a promising material for high power optical frequency conversion in the near and mid-infrared regions. In this paper, we have studied the properties of $ZnSiP_2$ semiconductor using first-principles calculations within density functional theory (DFT) and calculated the band gap (E_g), dielectric constant, refractive index, absorption coefficients, bulk modulus (B), melting temperature (T_m), Debye temperature (θ_D), plasmon energy $(\hbar\omega_p)$, heat of formation $(-\Delta H_f)$. Our calculated values of these parameters are in fair agreement with the available experimental values and the values reported by different workers.

II. COMPUTATIONAL DETAILS

Using Cambridge Sequential Total Energy Package (CASTEP) simulation software, we have calculated various parameters of $ZnSiP_2$ material. The calculations are based on the local density approximation (LDA) with exchange-correlation Ceperley-Alders potential parameterized by Perdew-Zunger scheme, with Norm-conserving Pseduo-potentials using plane wave basis set cut-off at 400 eV. Optimized structure has been obtained by applying Broyden, Fletcher, Goldfarb and Shannnon (BFGS) schemes. For this method, crystal reciprocal-lattice and integration over the Brillouin zone have been performed using 5 x 5 x 2 Monkhorst-pack. During the geometry optimization, the total energy difference of $5x10^{-7}$ eV/atom, Hellmann-Feynman ionic force within 0.01 eV/A°, maximum stress within $0.02\ GPa$ and maximum displacement within $5x10^{-4}$ A° have been taken.

III. RESULT AND DISCUSSION

a. The electronic and band structure of $ZnSiP_2$

The tetrahedrally coordinated $ZnSiP_2$ semiconductor belongs to the space group $I\bar{4}2d$ (No. 122) with body-centered tetragonal structure having four formula units in each unit cell [1]. This chalcopyrite is analogous to III-V compounds and is a super-lattice of zincblende structure. The atomic positions of $ZnSiP_2$ crystal are Zn (0, 0, 0), Si (0, 0, 0 .5) and P (u, 0.25, 0.125), where u is the lattice constant. We have performed band structure calculation using local density approximation (LDA) method. The band structure of $ZnSiP_2$ is shown in Fig. 1, which shows that the calculated value of energy gap 0f $ZnSiP_2$ is 1.383 eV. This value of energy gap is obtained using LDA scheme, which is slightly less than the experimental value of 2.07 eV [5]. The calculated, experimental and reported values of energy gaps are listed in Table 1**.** Further, it is well known that the LDA method underestimates the value of energy gap [3]. To overcome this problem, a well known technique, called the scissor correction, is used [14] which makes the calculated value equals to

experimental value. Our calculated value of E_g is scissor corrected by 0.687 eV for LDA scheme.

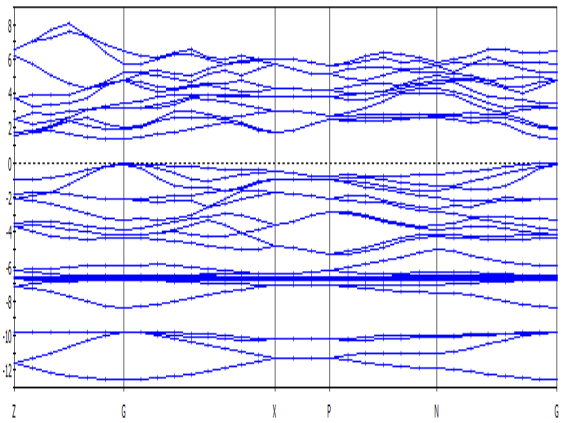

Fig. 1. Band structure of $ZnSiP_2$.

Fig. 2 shows the total density of state (TDOS) and partial densities of state (PDOS) for Zn-s/d, Si-s/p and P-s/p of $ZnSiP_2$ semiconductor. The PDOS signifies the angular momentum character, the orbital character and the states of hybridization of the semiconductor. The valence band maximum (VBM) is due to the presence of P-s/p, Zn-d, and Si-s/p, while conduction band minimum (CBM) is dominated by P-p and Si-p states, and little contribution of Si-s and P-s states. Further, the PDOS can be formally divided into three parts. The first part is from -12.8 eV to -9 eV which depends upon P-s and Si-s/p states, the second part is from -8.3 eV to Fermi energy (E_F), which are mainly due to the Si-p, Zn-d and P-p states, and finally the last part which comes under conduction band essentially dominated by P-p and Si-p states with minor presence of Si-s. From the Fig. 2, we can conclude that their exist a strong interaction between P-p and Si-p at around -3 eV.

The numerical value of plasmon energy $(\hbar\omega_p)$ of $ZnSiP_2$ semiconductor has been calculated from the loss function vs energy graph (see section III (B)), which comes out to be 15.95 eV against the reported value of

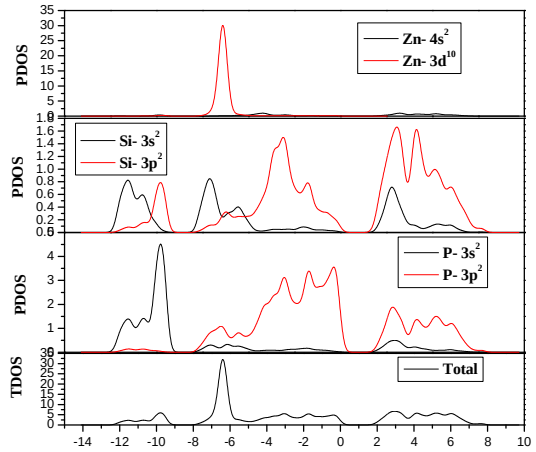

Fig.2. Total density of states (TDOS) and partial density of states (PDOS) of $ZnSiP_2$.

17.02 eV [12]. Using this value of plasmon energy (15.95 eV), we have further calculated the values of various parameters such as bulk modulus (B), melting point (T_m), Debye temperature (θ_D) and heat of formation $(-\Delta H_f)$ of $ZnSiP_2$ from the relations between $\hbar\omega_p$ and these parameters proposed by the author in their earlier publications [11,12,13]. The calculated values of these parameter are listed in Table 1 along with the experimental values and the values reported of different researchers. A fairly good agreement has been obtained between them.

Table 1: The energy gap (E_g), bulk modulus (B), melting temperature (T_m), Debye temperature (θ_D), plasmon energy $(\hbar\omega_p)$, heat of formation $-(\Delta H_f)$ of $ZnSiP_2$ semiconductor.
This work; [a]Ref 5, [b]Ref 13, [c]Ref 15, [d]Ref 16, [e]Ref 12, [f]Ref 17, [g]Ref 8.

Compd.	E_g (eV)	B (GPa)	T_m (K)	(θ_D) (K)	$(\hbar\omega_p)$ (eV)	$-(\Delta H_f)$	$\varepsilon_1(0)$	n(0)
$ZnSiP_2$	1.325* 2.07[a]	80.98* 79.00[c] 93.13[b] 88.00[d]	1250.8* 1572.6[e]	354.58* 444.79[e]	16.03* 17.02[b]	287.1* 307.8[f]	11.87* 11.24[g]	3.4* 3.4[d]

b. Optical properties

The optical properties such as refractive index $n(\omega)$, reflectivity $R(\omega)$, extinction coefficient $k(\omega)$, absorption coefficient $I(\omega)$, and energy loss function $L(\omega)$ of $ZnSiP_2$ material can be measured from complex dielectric function $\varepsilon(\omega)$. In the presence of electric field $\vec{E}$ the frequency dependent dielectric function $\varepsilon(\omega)$ is divided into two bands: the interband and the intraband transitions. The information related to the intraband transition is useful for the metals and the interband transition is useful for the semiconductors. The interband transition is further divided into two bands: the direct band and the indirect band transitions. With the help of momentum matrix elements between occupied and unoccupied wave functions, it is possible to calculate the direct interband contribution to the imaginary part of dielectric function $\varepsilon_2(\omega)$. The real part of dielectric function $\varepsilon_1(\omega)$ can be calculated using the following Kramer-Kroning relations:

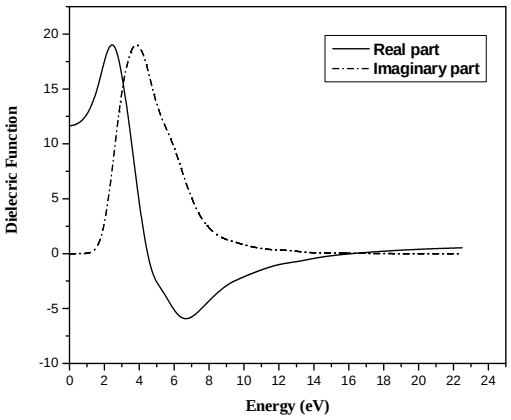

Fig. 4. Imaginary part $\varepsilon_2(\omega)$ (dash line) and real part $\varepsilon_1(\omega)$ (solid line) of the dielectric function of $ZnSiP_2$.

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi}\int_0^{\infty} \frac{\varepsilon_2(\omega)\omega' d\omega'}{\omega'^2 - \omega^2} \qquad (6)$$

$$\varepsilon_2(\omega) = \frac{Ve^2}{2\pi m^2 \omega^2}\int d^3k \sum_{nn'} \left|\langle kn|p|kn'\rangle\right| f(kn) \times [1 - f(kn')]\delta(E_{kn} - E_{kn'} - \hbar\omega) \qquad (7)$$

Figure 4 shows that the real and imaginary parts of dielectric constant, the real part $\varepsilon_1(0)$ = 11.87 for $ZnSiP_2$ against the reported value of 11.24 [8]. The calculated value of $\varepsilon_1(0)$ is found to be slightly higher in comparison to the theoretical value listed in Table 1. It is well known that experimental dielectric constant is absolute sum of electronic dielectric constant and lattice dielectric constant, and the lattice term cannot be neglected due to the ionic character present in $ZnSiP_2$. Also according to the Penn model, the static dielectric constant,

$\varepsilon_1(0) = 1 + (\hbar\omega_p / E_g)^2$.

This shows that the real part of dielectric function strongly depends on the energy gap of the semiconductor. The calculated energy gap is smaller than the experimental value due to the well known behavior of LDA method. Therefore, it is obvious that the calculated dielectric constant is slightly higher than the theoretical value. From the dielectric function, all other optical Properties

$n(\omega), R(\omega), k(\omega), I(\omega)$, and $L(\omega)$

are expressed by previous researchers [4]. The calculated result of refractive index is shown in Fig. 5. The theoretical and experimental refractive indices of crystals are also listed in Table 1. The calculated values are in good agreement with experimental results.

For the calculation of absorption spectrum, reflectivity, extinction coefficient and energy-loss spectrum curves are plotted in Fig. 6 (a)-(d)**.** In these calculations we have considered the case of the absorption spectrum shown in Fig. 6(a), the incident radiation with the linear polarization along the [10 0] direction with smearing 0.5eV. Absorption spectrum shown in Fig. 6(a) explains the decay of light intensity in unit distance. The absorption edge is located at 4.2eV and rapidly decreases in the lower nergy band, which is well known behavior of semiconductors and insulators. The energy-loss function tells about the energy-loss of a fast electron traversing in the semiconductor. The point at which highest loss-function occur, i.e. 16.03 eV which corresponds to plasmon energy as shown in Fig. 6(d) and listed in Table 1**.**

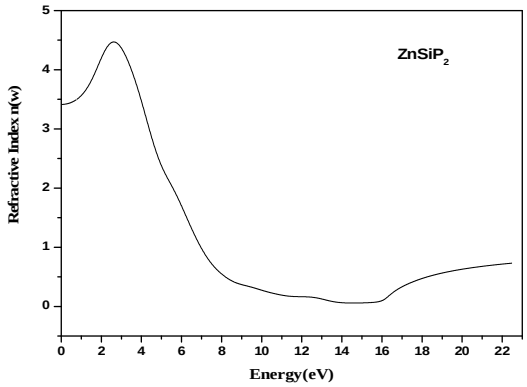

Fig. 5. Refractive index of $ZnSiP_2$.

At this point real and imaginary part of dielectric function is almost zero and corresponds to the trailing edge of Reflectivity spectra $R(\omega)$.

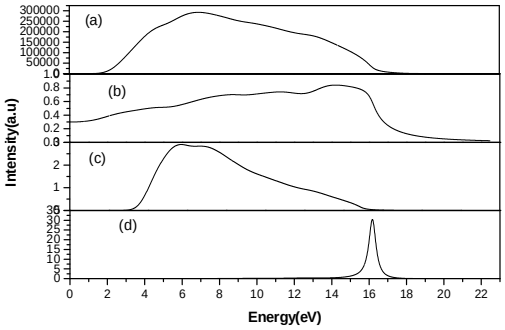

Fig.6. Optical constants of ZnSiP2: (a) absorption spectrum, (b) reflectivity, (c) extinction coefficient and (d) energy-loss spectrum.

CONCLUSION

The structural, electronic and optical properties of $ZnSiP_2$ compound have been calculated using CASTEP simulation software. We have performed first-principle calculation which is proven to be most accurate method for the computation of electronic structure of solids. The values of band gap, bulk modulus, heat of formation, Debye temperature, dielectric constant, refractive index and energy-loss spectra are in good overall agreement with the experimental values and the values reported by earlier researchers. So, the proposed theoretical calculations give a better agreement with the experimental values than the values proposed by earlier workers, which shows the soundness of the present simulation.

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