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Density functional theory study of structural, electronic and optical properties of ZnGeP2

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Abstract
First principles calculation within density functional theory (DFT) has been used to calculate the structural, electronic and optical of ZnSiP2 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 and loss function have been presented in energy range of 0-25 eV. The calculated values of these parameters are in good agreement with the experimental values and the value reported by previous researchers.

Keywords: ZnGeP2, electronic and optical properties

1. Introduction
The tetrahedrally coordinated ZnGeP2 semiconductor is a promising material having chalcopyrite structure with (I42d: 122) space group [1]. It has high nonlinear optical coefficient (d36 = 75 pm/V) and sufficient birefringence, very high melting point (Tm = 1027 C), enough thermal conductivity (=0.35 W/cm K) and high hardness, which allow its ap- plications in the fields of nonlinear optical (NLO) devices, high power optical parametric oscillators (OPO), frequency doublers and phase matching by angular tuning. Among the useable materials for frequency conversion in infrared regions, ZnGeP2 is the best known material which exhibits good transparency between 0.7 and 12µm wavelength regions. There have been various experimental and theoretical approaches to explain the electronic, optical and elastic properties of ZnGeP2 semiconductor. Several researchers have carried out experi- mental work on the growth of ZnGeP2, optical properties and defect in this semiconductor. The first-principle calculations have been performed to explain the electronic, elastic and optical properties of ZnGeP2 semiconductor.

2. Computational Details
We have performed the first-principle calculation using GPAW package [2] and ASE interface. The calculation are based on local density approximation (LDA) exchange correlation. Projector augmented wave [3] have been used with plane wave basis set cut-off at 600 eV. The crystal reciprocal-lattice and integration over the Brillouin zone have been performed using 4x4x3 Monkhorst-pack [4]. During the optimization of geometry,

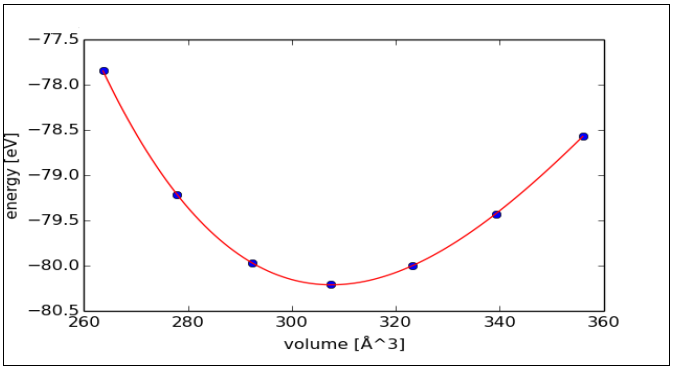

Fig 1: Total Energy vs Volume of ZnSiP2

Hellmann-Feynman ionic force of 0.01 eV/A, maximum stress of 0.05 GPa have been used. Optimized structure has been obtained by applying Quasi Newton scheme for minimizing forces on atoms and Broy- den, Fletcher, Goldfarb and Shanno (BFGS) scheme [5] for minimizing stress in the unit cell.

3. Results and Discussion
A. Structural properties of ZnGeP2
The chalcopyrite semiconductors crystallize in the tetrago- nal structure at ambient condition with space group (I42d:122) and having four formula units per unit cell. The atomic positions of ZnGeP2 crystal are Zn (0,0,0), Ge (0,0,0) and P (u, 0.25, 0.125) where u is the internal structural parameter. The total energy versus volume curve has been plotted for the optimized structure parameter using local density approximation (LDA) method and shown in Fig. 1. The optimized lattice constants (a and c) and the internal structural

parameter (u) have been calculated and listed in Table I along with the theoretical and experimental values [6, 7, 8]. Further, we have fitted the total energy versus volume data in Birch-Murnaghan equation of state (EOS) [9] to obtain the values of bulk modulus (B). The obtain result are in good agreement with the available experimental and reported values [10, 11, 12].

B. Electronic Properties

1) Band structure: Bloch theorem [19] states that the single-particle electronic wave functions in a crystal can be expressed.

Table 1: Calculated lattice constant (a and c), internal param-eter (u),energy gap(Eg), bulk modulus(B) of ZnGeP2

	Lattice parameter (Å)	u	E_g(eV)	B(GPa)
This work	a=5.378, c=10.634	0.249	1.426+ 1.536#	94.279* 85.98**
Expt. values	a=5.465[a], c= 10.700[a] a=5.463[b], c=10.740[b]	0.267[a]	1.99[c] 2.05[d]	79.3()17[e] 74.60[f]
Theoretical values	a=5.502[g], c=10.850[g]	0.254[g]	1.16[h] 1.079[i]	88.35[k] 79.30[l]

a Ref. [7]; b Ref. [8]; c Ref. [15]; d Ref. [16]; e Ref. [17]; f Ref. [12]; g Ref. [6]; h Ref. [13]; i Ref. [18]; k Ref. [10]; l Ref. [11];
Using LDA exchange-correlation; # Using PBE exchange-correlation;
#Calculated from EOS;
calculated from Voigt- Reuss-Hill method.

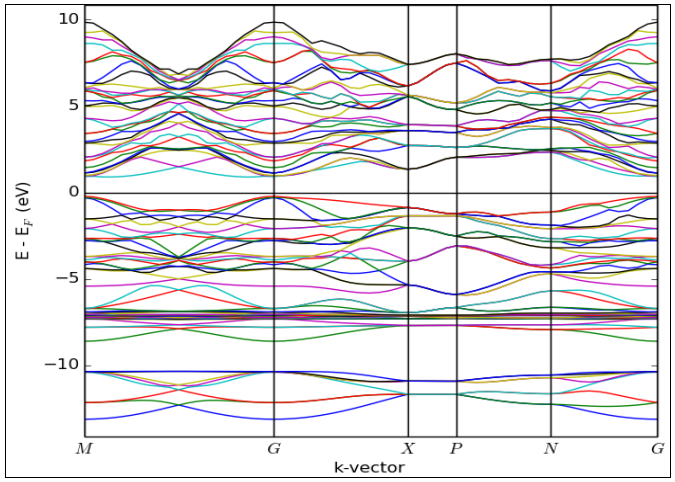

Fig 2: Bandstructure of ZnGeP2

As the product of a function periodic in the unit cell and a plane wave:

$$\varphi_i(\mathbf{r}) \rightarrow \varphi_{i\sim k}(\mathbf{r}) = e\, u_{\sim k}(\mathbf{r}) \quad (1)$$

Where

$$u_{i\sim k}(\mathbf{r}+\mathrm{T}) = u_{i\sim k}(\mathbf{r}), \quad \text{with} \sim \mathrm{T} = n_1 \cdot a_1 + n_2 \cdot a_2 + n_3 \cdot a_3 \quad (2)$$

and ~a1, ~a2 and ~a3 are primitive lattice vectors. Thus the one- electron wave functions can be indexed by constants k, which are the wave vectors of plane waves, a plot of the electron energies versus k is known as the electronic band structure of the crystal.

The single-particle Kohn-Sham equations are:

$$-\frac{1}{2}\nabla^2\phi_i(\vec{r}) + V_{tot}(\vec{r})\phi_i(\vec{r}) = \varepsilon_i\phi_i(\vec{r}) \quad (3)$$

$$V_{tot}(\vec{r}) = V_n(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r}) \quad (4)$$

Replacing the φi as defined by Eq. 1 and multiplying both sides by e−ι~k.~r finally result in

$$\left[-\frac{1}{2}(\nabla + i\vec{k})^2 + V_{tot}(\vec{r})\right] u_{i\vec{k}}(\vec{r}) = \varepsilon_{i\vec{k}} u_{i\vec{k}}(\vec{r}). \quad (5)$$

In this 'crystal' version of the Kohn-Sham equations the complex exponential term e(ι~k.~r) disappeared, and the function to be determined is only the periodic part, u, of the Kohn Sham state. One can state this result that the periodic part of the Kohn-Sham wave function is an eigen state of a modified Hamiltonian, Hˆ~k

$$\hat{H}_{\vec{k}} u_{i\vec{k}} = \varepsilon_{i\vec{k}} u_{i\vec{k}}, \hat{H}_{\vec{k}} = -\frac{1}{2}(\nabla + i\vec{k})^2 + V_{tot} \quad (6)$$

The numerical solution of Eq. 5 will require the description of ui~k on a discrete mesh points spanning only one unit cell. due to periodic nature of crystal. In reciprocal lattice it turns out that solution of Eq. 5 for Hˆ K~ +G~ with ~G a reciprocal vector, are simply duplicates of the solutions for Hˆ K. This observation allows us to restrict the 'useful' range of wave vectors ~ K to the first Brillouin zone. Actual calculation of band structure consists of two steps. First, the electron density is determined self-consistently. Once the ground-state density, n(~r), and the associated Kohn-Sham potential, Vtot, have been obtained, the Hamiltonian in Eq. 6 is completely specified. At this point one sweeps the wavevector, ~k solved in order to determine the eigenvalues εi~k, i = 1, 2, 3,... This second step is typically referred to as a 'non-self- consistent calculation', meaning that the electron density and the total potential are now left unchanged. When the discrete eigenvalues ε1~k, ε2~k,... are calculated for each wavevector along a given path are joined together, a continuous dispersion plot emerges. The curves thus obtained are referred to as bands, and entire plot is called band structure.

As shown in Table I the calculated value of bandgap along the Γ−Γ direction at G point is 1.426 eV using LDA and 1.536 using PBE, which is better than the earlier reported values of 1.16 eV [13, 14] against the experimental values of 1.99 eV [15] and 2.05 eV [16]. The value of band gap obtained using LDA scheme is 25% lesser than the experimental value. The LDA method is known for underestimating the values of band gap and is due to the discontinuity of exchange and correlation energy.

2) Density of State: The total density of state (DOS) and partial density of state (PDOS) plays important role to explain the physical properties of semiconductors. The PDOS and TDOS Zn-s/p/d, Ge-s/p/, P-s/p of ZnGeP2 are shown in the

Fig. 3 signifies that the origin of valence band and conduction band lies in local atomic states of constituents atoms. The PDOS further signify the angular momentum character, the local orbital character and of hybridization of the semiconductor. The Fermi energy is set to zero. The valence band region of ZnGeP2 from -15 eV to Fermi energy level Ef. can be divided into three sets: as low-, intermediate- and high energy. Sets of bands. The low energy sets of valence band ranging from -13.1eV to 10.7eV is mainly due to P-s state with the admixture of Ge-s/p states. The intermediate-energy set at 7.1 eV valence bands are mostly formed by Zn-d state. The higher- energy set extending from -5.65 eV to Fermi energy level is prevailing formed by P-p and Ge-p states with negligible contribution from Zn-s/p states. By analysing the states one can clearly observed that p-d hybridization which modifies the energy gap of material. Hence the p-like states are pushed up and Zn-d like state are pushed down. The conduction bands. From 1.222 eV to 8.3 eV mainly derived from P-p and Zn-s/p states with sufficient contribution from Ge-s/p states.

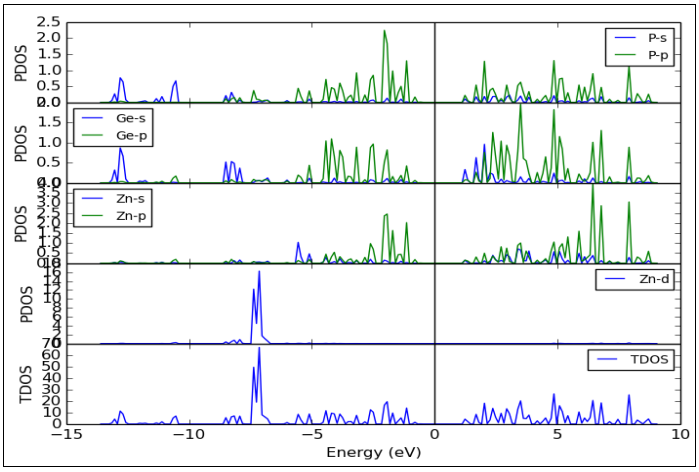

Fig 3: Total and Partial density of state of ZnGeP2

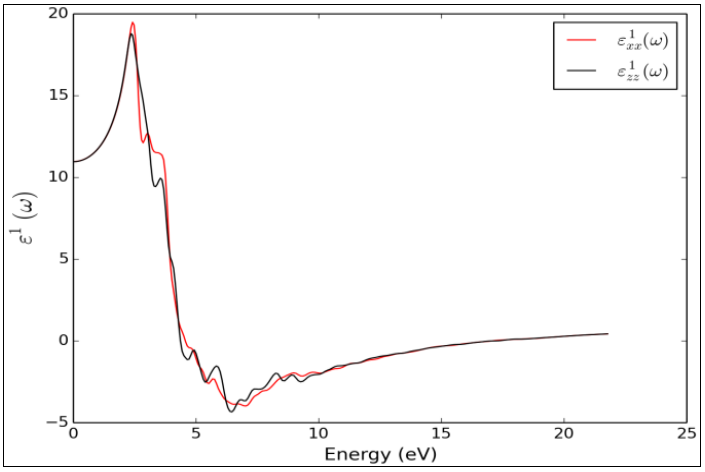

Fig 4: Real part of dielectric function of ZnGeP2

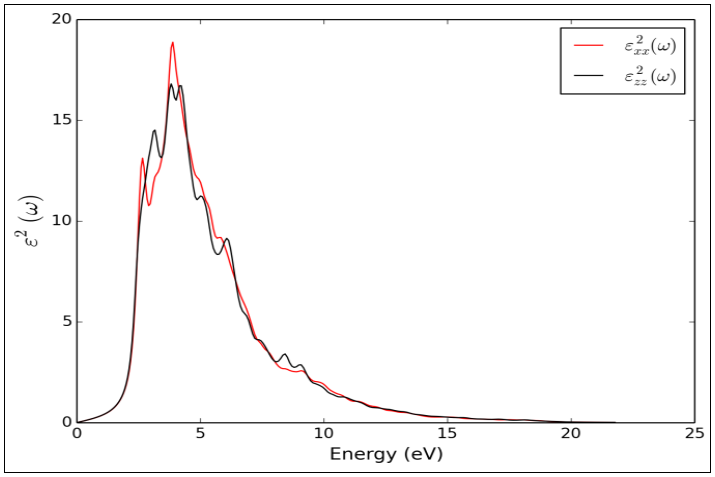

Fig 5: Imaginary part of dielectric function of ZnGeP2

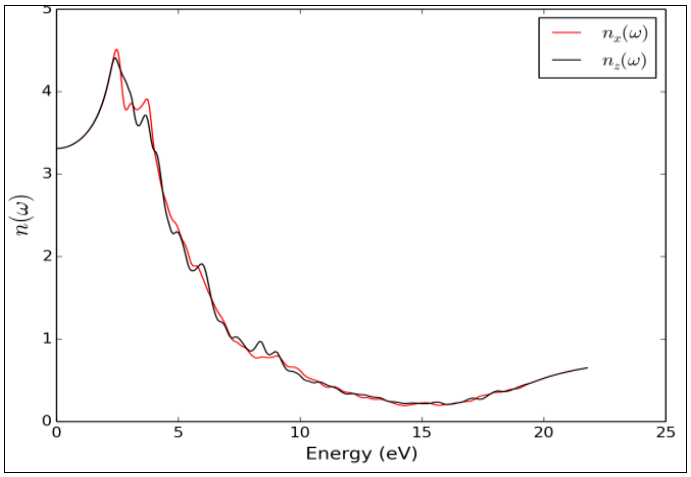

Fig 6: Refractive index of ZnGeP2

C. Optical Properties

To investigate the optical properties of ZnSiP2, the absorption coefficients, refractive indices, reflectivities and energy loss functions were calculated. The optical properties of a system can be described by the complex dielectric function, which is given by

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (7)$$

where ε1 is the real part of the complex dielectric function following the Kramer-Kroning equation and ε2 is the imaginary part.

From the dielectric function, all other optical properties such as refractive index n(ω), reflectivity R(ω), absorption coefficient α(ω), and energy loss function L(ω) can be expressed.

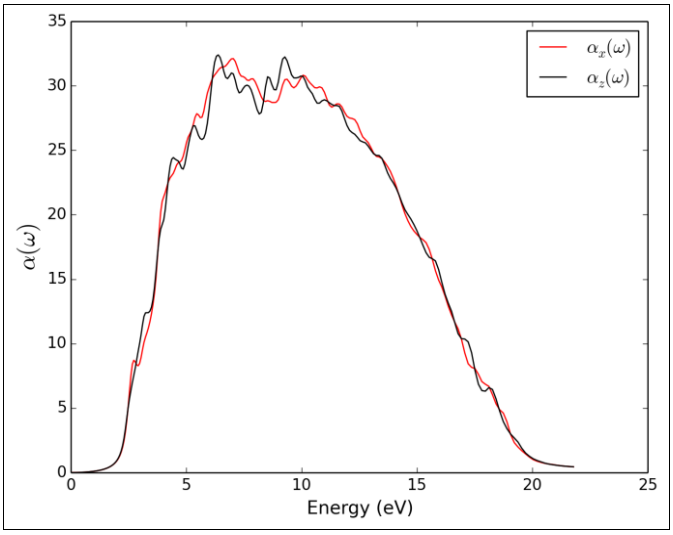

Fig 7: Absorbtion Coefficient of ZnGeP2

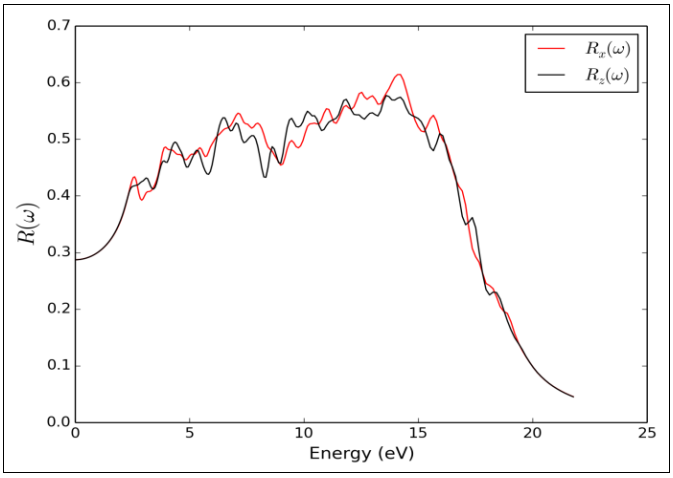

Fig 8: Reflectivites of ZnGeP2 2

The Absorption coefficient is proportional to the imaginary of complex index of refraction (extinction coefficient), so that K (ω) is usually associated with power loss. The fundamental aborbtion edge starts from 1.63 eV, and peaks lie at 7.03 eV in x-direction and 6.38 in z-direction as shown in Fig. 7. The curve for ZnGeP2 indicates an exponential variation in higher photon energy region. This trend is well-known as Urbach's rule [30] which has been observed for number of semiconductors and insulators. The energy-loss spectrum of ZnGeP2 is shown in Fig. 9, which tells about the energy-loss of a fast electron traversing in semiconductor. The point at which, highest loss-function occur, i.e (17.07 eV), corresponds to the plasmon energy ($\bar{h}\omega p$) of ZnGeP2 semiconductors. This is in close agreement with the reported value of $\hbar\omega p$ = 16.64 eV [10]. At this point, the real and imaginary part of dielectric constant are almost zero and correspond to trailing edge of R(ω).

4. Conclusion

In summary, the structural, electronic and optical properties of chalcopyrite semiconductor ZnGeP2 have been studied by means of DFT within the local density approximation (LDA). The most relevant conclusions are summarized as follows.

1. The calculated values of ground state parameters such as a, c, u and B are in good agreement with available experimental and theoretical values.
2. The energy gaps (Eg) along the Γ − Γ direction are in good agreement with the experimental values.
3. The optical properties such as dielectric constant ε1 (0), refractive index n(ω), reflectivity R(ω), extinction coefficient k(ω), absorption coefficient α(ω), and energy loss function L(ω) have been studied for both compounds.

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