Computational Investigation of Optical, Thermal and Thermoelectric Properties of Cs$_3$P compound

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Abstract. Electronic, Thermal, Thermoelectric and Optical Properties of Cesium Phosphide Cs$_3$P, are determined by means of Full-potential (FP) Linearized Augmented Plane Wave (LAPW) method using DFT (Density Functional Theory). Band structure, Density of States and Principle Optical constants of the compound were calculated. The computed Band gap and DoS (Density of States) histograms of the compound are agree well with the experimental studies and are similar to the compound used as reference which has been previously studied.

1. Introduction

The compound Cs$_3$P has high quantum efficiency and therefore has technological applications as a semiconductor. Theoretical research into this compound is necessary to understand the full potential of its applications. Understanding the electronic structure of this compound will aid substantially. In order to understand the photo emissive property of this compound knowledge from a theoretical aspect of the electronic structure is essential. Therefore using an already researched compound, Cs$_3$Sb as reference, a theoretical study into this compound has been conducted. The computations are done using FP-LAPW method [1]. Reference compound selected for this study Cs$_3$Sbhas been researched extensively and the results of this study can be applied for this particular study. The crystal structure of the compound Cs$_3$P is similar to the reference compound, thus the structural parameters of the reference compound is used for the initial calculations [3]. Cesium based compounds show promising technological applications as opto-electric devices. The optical properties of the compound can be known by evaluating the optical spectra. The spectrum of optical properties are limited to the inter band Brillouin zone transitions. Optical constants such as dielectric constant, absorption coefficient and optical conductivity are calculated.

Section 2 details the crystal structure of the compound. In Section 3 the results of the study is discussed and in the Section 4 the conclusions are presented.

2. Crystal Structure

The compounds crystallize in cubic structure. They belong to the space group Fm-3m (No.225). From the simulated image of the compound, Fig 1 it can be noted that the pnictogen atom,P is at the first sub-lattice and the Cesium atoms occupy the remaining sub-lattice. This is consistent with previous studies. The Phosphorous atom is situated at the centre of the structure and at the corners, whereas the Cesium atoms are at the face of the lattice structure and (3/4)a from the centre along the body diagonal.
calculations in the study are done using WIEN 2K code. The Lattice Parameters and structural parameters of the reference compound are used as input for Cs₃P. Using the initial parameters Volume optimisation is done, rendering a new optimised lattice parameter. This optimised parameter is used as input to study the optical and thermal properties of the compound. Along with the optimised lattice parameter, Bulk modulus B is obtained as a result of volume optimisation. Table 1 presents the initial parameters [4] and optimized volume and Bulk modulus obtained from Birch Murnaghan equation are listed in Table 2.

| Table 1. Lattice Parameter of Cs₃P |
|-----------------------------------|
| Compound Name | Space group | Lattice Parameter |
|----------------|-------------|-------------------|
| Cs₃P           | Fm-3m (No.225) | 9.128 Å          |

| Table 2. Optimised Parameters of the Compounds |
|-----------------------------------------------|
| Compound name | Optimised Lattice Parameter V₀ (a.u)³ | E₀ Ryd | Bulk modulus B (Gpa) | Pressure derivative B₀ |
|----------------|----------------------------------------|--------|----------------------|------------------------|
| Cs₃P           | 8.8047 Å³                              | -47425.91 | 7.6585 | 1.0190 |
| Cs₃SbParent/Reference compound [4] | 9.3407 Å³ | 1374.9180 | -59709.05 | 9.8071 | 4.5864 |

V₀ is the volume at the equilibrium pressure and E₀ is the corresponding energy. The values presented in the table 2 were obtained from Birch – Murnaghan equation of states by plotting total energy and volume of the compound. Values of the reference compound are used to compare due to the inexistence of previous studies for Cs₃P.

![Crystal Structure of Cs₃P](image)

Figure 1. Crystal Structure of Cs₃P

3. Results and Discussion

3.1. Electronic Structure

Band Structure and DOS of the compound are calculated for the optimized parameters. The theoretical band structure that has been calculated and the density of states associated with it for the Cs₃P are depicted in Fig 2 and Fig 3. Previous studies note that the electronic structure of the reference compound Cs₃Sb is mainly influenced by the overlapping Sb orbitals [3], [8]. This can be observed for the compound Cs₃P, where the P orbitals influence the electronic structure. The Fig 2 illustrates the band structure of the compound Cs₃P. Eₚ is the Fermi level and it is at 0.36 Ry. The deep valence band of the compound is the lowest line of the graph and it is the s state of phosphorus atom. As for the
compound Cs₃P, from the figures mentioned it can noted that the valence band is conquered by the s and p orbitals of P. The lowest energy (valence) band of Cs₃P is 3s orbital and it is localized around -0.5 Ry. The main contribution to the valence band is made by p state of Phosphorous. From the Fig 3 the direct band gap of Cs₃P for this study can be estimated by calculating the difference in maximum valence (lowest) band energy and minimum conduction (higher) band energy. The Band gap calculated for the compound Cs₃P in this study is 0.952 eV. Band gap estimated for the understudied compound and the reference compound is detailed in Table 3.

Table 3. Band gap of the compounds

| Compound name          | Calculated Band gap energy(eV) | Band Gap in Rydberg (Ry) |
|------------------------|-------------------------------|--------------------------|
| Cs₃P                   | 0.952                         | 0.07                     |
| Cs₃SbParent/Reference Compound [3] | 1.36                  | 0.1                      |

The Band (Eg) gap of the reference compound Cs₃Sb has been calculated at 1.6 eV [3]. The band gap calculated for Cs₃P in this study suggests that it is a semiconducting material. Additionally the band structure plots and DoS histograms for the reference compound were also calculated in this study in order to compare it with Cs₃P. Sb being the heavier element and higher atomic number had the presence of d orbital, other than that both compound showed similarities in band structure plots and DoS histograms as expected and are consistent with previous studies of the reference compound.

3.2. Optical Properties

The dielectric function \[\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)\] of the proposed compound is described from the optical properties, which is performed by using WIEN 2K code. The dielectric function has two parts, real \(\varepsilon_1\) and imaginary \(\varepsilon_2\). The imaginary dielectric function \(i\varepsilon_2(\omega)\) depict the absorptive part of the optical property. The absorptive part of the dielectric function \(\varepsilon_2\) of the compound Cs₃P is shown in the Fig 4. Each spectrum are decomposed and deconstructed into pairs of contribution and analysis of the origin of different peaks is done on this basis. This allows the identification of microscopic origin...
optical spectrum characteristics and explains the Brillouin zone contributions at various K-points. The main contribution to the optical spectra originates from the transition of electrons from the valence band into bottom three conduction bands.

From the Fig 4 it can be observed that the threshold in $\varepsilon_2$ (imaginary) is around 1.15eV and it is created by the direct gap caused by $v_1$-$c_1$ and $v_2$-$c_2$ transitions. The exponential rise after reaching the first peak at 1.86 eV is caused by the strong valence to conduction band transition with respect to energy gap ($v_1$-$c_1$ and $v_2$-$c_1$ transitions). There are four main contributions in the energy ranges In in between 1.75–2.5 eV, are (i) the $v_1$-$c_1$ transition, (ii) the $v_2$-$c_1$ ii) the $v_1$-$c_2$ transition and(iv) $v_2$-$c_2$ transition. The peak structures above 3.0 eV arise due to the v3-c3 and v3-c1 transitions.

Evaluating the peaks of the dielectric function, $\varepsilon_2$ and the corresponding Energy from the Fig 4 will explain the nature of transitions related to the optical spectra. Energy analogous to the various peaks of the Dielectric [$\varepsilon(\omega)$] function of the reference compound is compared with the understudied compound and is detailed in the Table 4. From the table it can be seen that both compounds are optically similar. Fig 5 illustrates the dielectric function [$\varepsilon(\omega)$] real part to the energy relation. From the figure the inactive dielectric constant $\varepsilon_1(0)$ can be evaluated and it is a very important quantity determining a materials semiconducting property. The value of $\varepsilon_1(\omega)$ at zero energy is the static dielectric constant $\varepsilon_1(0)$. $\varepsilon_1(\omega)$ has negative values between 2.625 eV and 5.75 eV and above 12 eV. This negative value of $\varepsilon_1$ indicates that the incident electromagnetic waves are entirely reflected. As the function approaches zero at 12.0 eV, there are no transitions after this value. The peak value of $\varepsilon_1(\omega)$ is 13.0 and the energy corresponding to it is 1.375 eV. The specific values of the Dielectric [$\varepsilon(\omega)$] function real part for the compound Cs$_3$P is noted in the Table 5 along with the reference compound Cs$_3$Sb.

Table 4. Values of the dielectric function (Imaginary)

| Compound | Threshold value of $\varepsilon_2$ eV | Shoulder region Range eV | Value of Energy at Main Peak eV |
|----------|--------------------------------------|--------------------------|-------------------------------|
| Cs$_3$P  | 1.15                                 | 1.75-2.5                 | 2.55                          |
| Cs$_3$Sb | 1.0                                  | 1.25-2.0                 | 2.28                          |

Parent/Reference Compound [3]
Figure 5. The dielectric function

Table 5. Values of the dielectric function (Real)

| Compound | \( \varepsilon_1(0) \) | Energy range for negative \( \varepsilon_1(\omega) \) eV | Static value of \( \varepsilon_1(\omega) \) | Energy corresponding to the static \( \varepsilon_1(\omega) \) eV |
|----------|---------------------|---------------------------------|-----------------|------------------|
| Cs_P     | 8.6                 | 2.60-5.725, 12.10-14.0          | 13.0            | 1.375            |
| Cs_Sb    | 8.3                 | 2.50-5.50 12.25-14.0           | 12.0            | 1.577            |

3.2.1. Optical Conductivity. Optical Conductivity \( \sigma(\omega) \) describes the conduction of free charges over a particular range of Photon energy. Fig 6 represents the optical conductivity of Cs_P, \( \sigma \) in terms of the energy. The main peak of \( \sigma(\omega) \) is at 12.5 eV. There are 3 major peaks for Fig 6, these points exhibit excitonic feature, at 2.5, 12 and 12.5 eV. Excitons are bound electron-hole pair and they move around the crystal transporting energy, the sudden peak in the optical conductivity is caused by the excitons. The main peak of the function \( \sigma(\omega) \) for the compounds from the figure corresponds to the maximum optical conductivity \( \sigma_{\text{max}}(\omega) \). The value of \( \sigma_{\text{max}}(\omega) \) for Cs_P is 6928.57. Along with maximum optical conductivity, the static value of reflectivity \( R(0) \) and refractive index \( n(0) \) for the compound under study here is noted in the Table 6 along with Cs_Sb. The static values of reflectivity and refractive index are reported here, the graphs from which they were obtained are included in the thesis report.

3.2.2. Absorption coefficient. Cs_P can be used as photo-emitters since, its visible region in spectrum of electromagnetic region has efficient optical absorption. The coefficient of absorption for the compound is displayed in the Fig 7. Within the energy range 0-6 eV. The compound shows a relatively strong structure above 2.5 eV with peaks at 3.25 eV and 4.75 eV and minima at 4 eV. The theoretical spectrum is not broadened and hence the absorption coefficient with in the energy range 0-6 eV is taken into consideration. The absorption coefficient is denoted by the symbol \( \alpha \) and the unit
is cm$^{-1}$. The theoretical absorption curve of the parent/reference compound Cs$_3$Sb compares well with the experimental one [9].

| Compound name       | n(0) | $\sigma_{\text{max}}$ ($\omega$) | R(0) % |
|---------------------|------|----------------------------------|--------|
|                      | n$_{\text{refractive}}$ index |                                  |        |
| Cs$_3$P              | 2.945 | 6928.57                          | 24     |
| Cs$_3$SbParent/ReferenceCompound [8] | 2.910 | 5819.54                          | 23.5   |

3.3. Thermal Properties

Gibbs free energy is used to determine thermodynamic stability of the compound by using the relation, $G= E+PV+TS$. $E$ is the internal energy of the system and $S$ is the entropy, the calculations for the above mentioned parameters are done using Gibbscode2. The thermodynamic properties are defined using Debye model and it is implemented in Gibbs code [11]. The Gibbs free energy vs T relation of the compound is illustrated in the Fig 8. It can be observed that the Gibbs energy is decreasing with the increase in temperature which confirms thermodynamic stability of the compound.

Some of the other factors that determine the thermal property of a material are Bulk Modulus, Debye temperature and Heat capacity [12]. Optimised Bulk Modulus of the compound was discussed earlier in Section 2, Table 2.
3.4. Thermoelectric Properties

Thermoelectric property of a material is an key factor in determining its energy conserving aspect and the materials ability to convert heat into electricity and vice versa. Some of the important parameters concerning a material’s thermoelectric property are Seebeck coefficient ($S$), Power factor and electrical conductivity. Seebeck coefficient is the proportionality constant or coefficient which relates induced voltage $d\Delta V$ with $\Delta T$. Power factor can be calculated by using Seebeck coefficient and electrical conductivity ($\sigma$). Power factor is the product of electrical conductivity and square of Seebeck coefficient and the same is represented by $PF=S^2 \times \sigma$. Fig 9 displays the relation of Seebeck coefficient with Temperature and Fig 10 relates Power factor with $T$ of the compound.

![Figure 9. Seebeck Coefficient vs T](image)

![Figure 10. Power factor vs T](image)

From the Fig 9 it can be observed that the temperature and Seebeck coefficient are inversely proportional to each other whether $S$ decreases when increasing temperature at low temperature range, after that it remains at almost constant values and the value of Seebeck coefficient value at 300 K is 242.81 $\mu$V/K, which is a relatively high value and suggests that the compound shows semiconducting property, since semiconductors have high $S$ value. Power factor rises consistently with increase in temperature and it has high values at higher temperatures. Power factor of a material determines its thermoelectric efficiency. Power factor of the compound at 300K is 1.812 Wm$^{-1}$K$^{-2}$ has relatively a high value and therefore the compound is thermoelectrically efficient.

4. Conclusion

In this paper the optical spectrum of the proposed compound namely $Cs_3P$, by using first principles study has been presented along with the study of thermal properties, thermoelectric properties and electronic structure. From analysing the available data, the compound, $Cs_3P$ is a semiconductor. It has the optimum band gap, optical conductivity and dielectric constant to be an opto-electric device. The Direct Band gap of $Cs_3P$ for this study has been approximated at 0.952eV. The optimized bulk modulus of the compound was calculated as well. In the absence of a previous theoretical study on this specific compound, another compound with similar characteristics was used for reference and comparing the results both compounds indeed show similar optical and thermal properties. The band structure and optical spectra calculated in this study are well agreed with the experimental study and the compound is found to be thermodynamically stable. The high values of Power factor suggest that the compound is thermoelectrically efficient.

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