First Principles Investigations on Structural, Elastic, Electronic, and Optical Properties of Li₂CdGeS₄

Weimin Peng¹, Xiaofeng Li¹,²,* and Junyi Du³

¹College of Physics and Electronic Information, Luoyang Normal College, Henan Luoyang, 471022, P. R. China
²Beijing Computational Science Research Center, Beijing, 100084, P. R. China
³Mathematics College, Luoyang Normal College, Henan Luoyang, 471022, P. R. China

First principles calculations have been carried out to investigate the crystal structure, elastic constants, chemical bonding, electronic, and optical properties of Li₂CdGeS₄. The calculated equilibrium lattice constants, bulk modulus and its pressure derivative are in reasonable agreement with the available experimental results. We have predicted the elastic constants as well as bulk and shear moduli. By the elastic stability criteria, it is found that Li₂CdGeS₄ is mechanically stable and is a ductile system. Electronic and chemical bonding properties have been studied through the calculation of band structure, density of states and Mulliken population. We found that the energy band gap is 2.817 eV in LDA (2.421 eV in GGA) for Li₂CdGeS₄. Moreover the complex dielectric function, refractive index, extinction coefficient, reflectivity and loss function are also calculated, which show significant optical anisotropies in the components of polarization directions (1 0 0), (0 1 0) and (0 0 1). [doi:10.2320/matertrans.M2013186]

(Received May 27, 2013; Accepted September 17, 2013; Published November 25, 2013)

Keywords: Li₂CdGeS₄, elastic constant, electronic structure, optical properties

1. Introduction

In the past few years, multi-cation diamond-like semiconductors (DLSs) have received a lot of attentions. It is due to their promising, tunable properties in varying the chemical composition, and thereby optimizing the material functionality. They may bring out more applications in the areas of photovoltaics, nonlinear optics, thermoelectricity, solar cells and light-emitting diodes. The researches on the quaternary I₂–II–IV–VI₄ compounds have been reported, especially Cu₂ZnGeS₄ has drawn much attention as being a promising candidate as absorber layer in solar cell technologies. However, there are only a few studies about Li₂CdGeS₄. Lekse et al.¹¹) reported that semiconductor Li₂CdGeS₄ was firstly synthesized in both single crystal and polycrystalline forms by high-temperature solid-state and polychalcogenide flux syntheses. They also proposed that the replacement of Cu by Li may enlarge the band gap of this compound, which may result in higher laser damage thresholds. Additionally, the presence of Li as the univalent cation allows for the use of a lithium polysulphide flux as a reaction medium to promote crystal growth. Li et al.¹²) investigated the electronic structure and lattice dynamic properties of Li₂CdGeS₄. We all know that the systematical information on the structural, elastic, electronic, optical and bonding properties of I₂–II–IV–VI₄ compounds are helpful to further understand the physical properties of semiconductors.

In this paper, the main aim is to give a detailed description of the Li₂CdGeS₄. It is as follows: (i) structural and elastic properties, (ii) electronic properties, such as the energy band structure, density of states, (iii) optical properties, such as the absorption, reflectivity, refractive index, and (iv) bonding properties, such as the Mulliken charge, overlap population. These results will provide much more useful information for diamond-like semiconductors.

*Corresponding author, E-mail: lxfdjy@126.com

2. Computation Method

In the electronic structure calculations, the non-local ultrasoft pseudopotential introduced by Vanderbilt¹³) has been employed for all the ion-electron interactions. The performed calculations included two exchange–correlation potential: one is the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof of Solid (PBESOL);¹⁴) the other is the local density approximation (LDA) with the Ceperley–Alder–Perdew–Zunger (CA–PZ).¹⁵) Pseudo-atom calculations are performed for Li 1s² 2s¹, Ge 4s² 4p², Cd 4d¹⁰ 5s² and S 3s² 3p⁴. The self-consistent convergence of the total energy is 5.0 × 10⁻⁷ eV/atom. To confirm the convergence of our calculations, we carefully investigate the dependences of the total energy on the cutoff energy and the Monkhorst-Pack grid. Considering the computational cost, a plane-wave basis set with an energy cutoff of 350 eV is applied, and 6 × 6 × 6 k-point Monkhorst-Pack mesh is used for the Brillouin-zone (BZ) k-point sampling. It is found that these parameters are sufficient for leading to well converged total energy. In the calculations of optical properties, the applied k-point in the Brillouin zone (BZ) is also 6 × 6 × 6. The non-local ultrasoft pseudopotential introduced by Vanderbilt¹³) is also adopted. Meanwhile, the number of conduction bands which determines the covered energy range and the accuracy of the Kramers-Kronig transform, is an important parameter in the calculation. In the present study, in addition to the occupied bands, 12 empty bands are included, and the electronic structure and optical properties are all studied by using the Cambridge Serial Total Energy Package (CASTEP).¹⁶,¹⁷)

3. Results and Discussions

Li₂CdGeS₄ is an orthorhombic crystal with space group Pmn2₁. We performed the total energy electronic structure calculations in the range of primitive cell volume V from 0.80V₀ to 1.20V₀, in which V₀ is the zero pressure equilibrium
primitive cell volume. The detailed calculations are depicted as follows: firstly, for a given $b$ the axial ratio $c/a$ is fixed and a series of different lattice parameters $a$ and $c$ are taken to calculate the total energies $E$. No constraints are imposed on $c/a$, i.e., both lattice parameter $a$, $c$ are optimized simultaneously. In the second step, the procedure is repeated over a range of ratio $c/a$. For given $b$, the minimum total energy $E$ is obtained by calculating the energy $E$ for each fixed axial ratio $c/a$; finally, we repeat two procedures above for different $b$, and then find the minimum total energy $E$ for each $b$. By fitting the $E$-$b$ data to third-order polynomial, we obtained the minimum energy of Li$_2$CdGeS$_4$. Meanwhile, the axial ratio $c/a$ with minimum total energy is also obtained. By fitting the calculated energy-volume ($E$-$V$) data to the three-order natural strain equation of state, the calculated lattice constants $a$, $b$, $c$, $V_0$, bulk modulus $B_0$ at zero pressure and its pressure derivative $B'_0$ with available experimental and theoretical data for Li$_2$CdGeS$_4$ are summarized in Table 1, which shows that the calculated values of GGA calculation are in better agreement with the experiments than that of LDA calculations. Unfortunately, there are no experimental value of bulk modulus and its pressure derivative for comparisons. Elastic properties of solids are important for understanding interatomic potentials and relate to various fundamental solid state phenomena as well as specific heat, thermal expansion, the Debye temperature and the Gr"uneisen parameter. In particular, they provide information on the stability and stiffness of materials. For an orthorhombic crystal Li$_2$CdGeS$_4$, there are nine independent elastic constants, i.e., $C_{11}$, $C_{22}$, $C_{33}$, $C_{44}$, $C_{55}$, $C_{66}$, $C_{12}$, $C_{13}$ and $C_{23}$. These elastic stiffness coefficients can be determined by computing the stress generated by forcing a small strain to an optimized unit cell. The elastic constants, bulk modulus $B$ and shear modulus $G$ of Li$_2$CdGeS$_4$ at 0 K and 0 GPa are displayed in Table 2. It can also be seen that LDA gives larger elastic constants than GGA. This may be due to the smaller lattice parameters predicted in LDA than in GGA. Unfortunately, there are no theoretical and experimental results for comparing with the present work. Then our results can serve as a prediction for future investigations.

For the orthorhombic crystal, its mechanical stability, which depends on its independent elastic constants, is judged from the Born stability criteria:

\[
C_{11} + C_{22} - 2C_{12} > 0, \quad C_{11} + C_{33} - 2C_{13} > 0, \\
C_{22} + C_{33} - 2C_{23} > 0, \quad C_{ij} > 0, \\
C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0
\]

Obviously, the calculated elastic constants $C_{ij}$ (Table 2) satisfied all the restrictions, implying that Li$_2$CdGeS$_4$ is mechanically stable. In the present calculations, $C_{11} > C_{33}$, indicating that the bonding strength along the [100] and [010] direction is stronger than that of the bonding along the [001] direction. $C_{44}$ is approximately equal to $C_{66}$, which suggests that the [100] (010) shear is closed to the [100] (001) shear. The [ijk] and (ijk) denote symmetry axis and plane, respectively. Moreover, from Table 2 it can be seen that $B/G$ is 2.472 of GGA result (3.159 of LDA result) which is larger than the critical value (1.75) separating ductile and brittle materials. The result indicated that Li$_2$CdGeS$_4$ is a ductile material.

The calculated energy band structures of Li$_2$CdGeS$_4$ along the high-symmetry points of the Brillouin zone by GGA and LDA are shown in Fig. 1. There is a direct band gap at $G$ point for Li$_2$CdGeS$_4$, which is 2.82 eV in LDA result (2.42 eV in GGA). However, it is found the indirect energy band gap at G-X point in Ref. 12). It is due to the fact that the band gap value between the G-G and G-X point is very close. Moreover, the non-local ultrasoft pseudopotential in present calculation is employed, the norm-conserving pseudopotential was applied in Ref. 12). Therefore, the energy gap is different from that depicted in Ref. 12). The calculated band gap of LDA result agrees with the previous theoretical value (2.83 eV), but is smaller than the experimental value 3.10 eV due to the well-known underestimation of conduction band state energies in DFT calculations. In Table 3, we collected the direct and indirect band gaps and compared them with experimental and theoretical ones. From Table 3, we can find that the band gap in LDA is larger than that in GGA, it is perhaps due to the smaller lattice constants predicted in LDA and the difference of methods in LDA and GGA which deal with the electron density.
The investigation of the nature of the electronic band structure requires the knowledge of partial and total density of states. The total and partial density of states of Li₂CdGeS₄ (TDOS and PDOS, respectively in GGA and LDA) are shown in Fig. 2 for the energy range from −45 to 10 eV. The overall TDOS and PDOS profiles are in good consistent with the previous theoretical calculation.¹² It is observed that, the lowest valence band (−45 to −20 eV) is mainly contributed by Li-s state; the higher valence band about −20 to −10 eV originate from the Ge-s/p states and S-s state, which have a little contribution by Cd-p state. The higher valence band (−10 to −5 eV) mainly stems from the hydriizations of Cd-d state, S-p state and Ge-s state; the bands located in −5 to 0 eV is owing to the contribution of Cd-s/p states, Ge-s/p states and s-p states; the conduction bands above the Fermi level are almost dominated by Ge-s/p states, Cd-s state and S-p states. The obtained results are a little different from that in Ref. 12), which may be due to using different pseudopotential.

As usual, the relative strength of the chemical bonds among the atoms could be evaluated by the Mulliken charge and overlap population.²² Moreover, the effective valence is used to determine the dominance of either covalent or ionic bonding. The effective valence of the perfectly ionic bond is zero, whereas the corresponding valence is greater than zero when the bond is covalent. Table 4 presents the total and effective valence charges of Li, Cd, Ge and S species Li₂CdGeS₄. The charges transferring from Li, Ge and Cd to S are about 0.94e, 0.77e and 0.19e, respectively (0.87e, 0.80e and 0.32e in GGA). Therefore, it concluded that the bonding behavior of Li₂CdGeS₄ is a coexistence of covalent and ionic natures. Moreover, the Cd–S bond possessed a stronger covalent bonding strength than Li–Ge–S bonds. The calculated results of the Mulliken bond populations and bond lengths in Li₂GeCdS₄ using both GGA and LDA functions are also shown in Table 4. The positive and negative value of bond populations represent the bonding and antibonding states, respectively. The Mulliken bond population of the Cd–S bonds (LDA) is in the range 0.47–0.56 Å (0.42–0.49 Å with GGA), which is smaller than the range 0.72–0.84 Å for the Ge–S bonds. These results agree with the analysis of electronic structures and density of states above.

To further understand the physical properties of Li₂CdGeS₄, the optical properties are also investigated, which include many physical parameters, such as the frequency-dependent complex dielectric constant \( \varepsilon(\omega) \). The
electron energy loss function $L(\omega)$, the refractive index $n(\omega)$, the absorption coefficient $k(\omega)$, the reflectivity coefficient $R(\omega)$, the extinction coefficient $k(\omega)$ and so on. The optical properties have been obtained through the calculation of the frequency-dependent dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$, using the formalism of Ehrenreich and Cohen. The imaginary part $\varepsilon_2$ of the dielectric function are available by evaluating the matrix elements of the electric dipole operator between the occupied and unoccupied electronic states in the valence band (including the deeply located bands as well) and conduction band, respectively. The real part $\varepsilon_1$ of the dielectric function is obtained from the Kramers-Kronig transform.

For optical properties of Li$_2$CdGeS$_4$, we considered three polarization planes (100), (010) and (001), which denotes the crystalline direction parallel to the polarization vector. The calculated dielectric function of Li$_2$CdGeS$_4$ is shown in Fig. 3 (due to the similarity of the profiles of DOS with GGA and LDA, the displayed optical properties are the results with LDA). It is found that the dielectric functions show a significant anisotropy from (1 0 0), (0 1 0) and (0 0 1). It can be seen that in a high-energy area (frequency larger than 8 eV), the values of the imaginary part are very small, while the real part changes very little for Li$_2$CdGeS$_4$. There is an obvious peak at 2.95 eV in real part, it is due to the direct energy band gap between the valence and conduct bands. The calculated static dielectric constants are 4.28, 4.02 and 4.05 eV from (1 0 0), (0 1 0) and (0 0 1) respectively. On the other hand, the imaginary part $\varepsilon_2(\omega)$ of the dielectric function is related to the absorption spectrum due to the electronic transitions from the valence band to conduct band. Several peaks are mainly regarded to the transitions from valence band to conduct band by comparing to their Density of states characteristics. However, one should note that a peak in imaginary part does not correspond to a single interband transition because many direct or indirect transitions contribute to each peak.

The absorption and reflectance spectra are exhibited in Fig. 4. From Fig. 4 we can easily found that the profiles of the reflection and absorption spectra are very similar to each other. It is means that, if a material can absorb light strongly in some range, it can also effectively reflect light in the same range. The calculated absorption coefficient of Li$_2$CdGeS$_4$ from (1 0 0), (0 1 0) and (0 0 1) are 2.68, 2.75 and 2.85 eV respectively, which is agreement with the analysis of energy band structure and experimental data. It can be observed that the absorption spectrum has an absorption peak in a low energy range. The strong optical absorption peaks appears mostly in the high energy region (6–8 eV), which corresponds to the interband transitions. However, the absorption decreases with the photon energy in a high

<table>
<thead>
<tr>
<th>Mulliken charge populations</th>
<th>Bond population</th>
<th>Bond length</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>p</td>
<td>d</td>
</tr>
<tr>
<td>Li</td>
<td>2.13 (2.06)</td>
<td>2.13 (2.06)</td>
</tr>
<tr>
<td>S1</td>
<td>1.87 (1.86)</td>
<td>4.85 (4.83)</td>
</tr>
<tr>
<td>S2</td>
<td>1.87 (1.86)</td>
<td>4.83 (4.86)</td>
</tr>
<tr>
<td>Ge</td>
<td>1.18 (1.14)</td>
<td>2.02 (2.10)</td>
</tr>
<tr>
<td>Cd</td>
<td>0.81 (0.87)</td>
<td>0.89 (0.97)</td>
</tr>
</tbody>
</table>

Fig. 3 The real part $\varepsilon_1$ and imaginary part $\varepsilon_2$ of the dielectric function for polarization vectors (100), (010) and (001) of Li$_2$CdGeS$_4$.

Fig. 4 The reflectivity and absorption spectra of Li$_2$CdGeS$_4$ for polarization vectors (100), (010) and (001).
energy range (above the 10 eV), where the electron is hard to respond.

The electron energy-loss function \( L(\omega) \) of Li\(_2\)CdGeS\(_4\) is displayed in Fig. 5, which is an important parameter describing the energy loss of a fast electron traversing in the material. The peaks in this spectrum represent the characteristic associated with the plasma resonance (a collective oscillation of the valence electrons) and the corresponding frequency is the so-called plasma frequency. It indicated that the transition from the metallic property \((\varepsilon_1 < 0)\) to the dielectric property \((\varepsilon_1 > 0)\) for a kind of material. In lower energy region, there are no obvious peaks which are consistent with the zero crossing of \(\varepsilon_1(\omega)\). The sharp peak in the \(L(\omega)\) is located at 9.85, 9.73 and 9.92 eV which correspond to the trailing edges of the reflection spectra shown in Fig. 4(b), when the reflectivity reduces sharply in higher energy region. Figure 6 shows the refractive index \(n\) and the extinction coefficient \(k\). The calculated static refractive indices \((n)\) are 2.04, 1.95 and 1.98 eV from (1 0 0), (0 1 0) and (0 0 1). The refractive index decrease with the increasing energy in the transparency region, reaching a local minimum at 0.85, 0.93 and 0.94 eV along the direction (1 0 0), (0 1 0) and (0 0 1), respectively. The extinction coefficient \(k\) increases with energy in the transparency region, reaching the peaks in the ultraviolet at about 6.85, 6.75 and 6.78 eV for (1 0 0), (0 1 0) and (0 0 1). It can be seen that the increase of extinction coefficient with the photon energy shows that the fraction of light lost due to scattering and absorbance decreases.

4. Conclusions

We have investigated the crystal structure, elastic constants, energy band structure, density of states, optical properties, and bonding properties of Li\(_2\)CdGeS\(_4\) using first principles calculations. The equilibrium lattice parameters, bulk modulus and its pressure derivative of Li\(_2\)CdGeS\(_4\) are optimized, and the calculated results by GGA and LDA are consistent with the experimental data and the available theoretical results. The elastic constants are firstly predicted by the methods of LDA and GGA. Our calculations reveal that Li\(_2\)CdGeS\(_4\) shows elastic anisotropy and elastic stability under ambient conditions. The calculated \(B/G\) value is 2.472 of a GGA result (3.159 of LDA result) which indicated that Li\(_2\)CdGeS\(_4\) is a ductile material. Our results for the band structures and DOS show that Li\(_2\)CdGeS\(_4\) is semiconductor with a direct band gap. The energy band gap is estimated to be 2.817 eV (LDA) or 2.421 eV (GGA), which are both underestimated and compared with the experimental band gap. Based on the calculations of the density of states and Mulliken population, the chemical bonding indicated both ionic and covalent bonding in Li\(_2\)CdGeS\(_4\). Our calculated reflectivity spectra, the imaginary parts and real parts of the dielectric function, the extinction coefficient, and the refractive index are in good agreement with the obtained experimental results.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 11304140), Program for Innovative Research Team (in Science and Technology) in University of Henan Province under Grant No. 13IRTSTHN020, the Henan Research Program of Basic and Frontier Technology under Grant No. 122102210390, the Henan Natural Science Basic Research under Grant No. 2011B140013.

REFERENCES