Opto-Electronic Properties of Li$_2$C$_2$ Polymorphs

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Abstract

The electronic and optical properties of Li$_2$C$_2$ in different structural phases are studied in the frame work of density functional theory. Full potential linearized augmented plane waves plus local orbitals (FP-LAPW+lo) method is applied within the Engel-Voskogeneralized gradient approximation. The compound is metallic in $Bmmb$ phase, while insulating in $Immm$ and $I2_1$3 phases. The calculated bandgaps are in close agreement with the previous predictions. The two phases $Immm$ $I2_1$3 and show a high dielectric function and optical conductivity in the UV range and are therefore suitable to be used in the fabrication of optoelectronic devices.

Keywords: Optical Conductivity; Fabrication; Optoelectronic devices; Bandgaps.

Introduction

Metal-intercalated graphite Li$_2$C$_2$ owing to its unique physical and chemical properties have been of scientific [1-3] and technological interest in the recent years. In a recent experimental study, the $Immm$ phase has been reported to be the thermodynamically stable phase of Li$_2$C$_2$under ambient conditions [1]. A previous density functional theory (DFT) based study of lithium carbide (Li$_2$C$_2$) predicted a pressure induced structural phase transition from orthorhombic ($Immm$) at 0 GPa $\rightarrow$ hexagonal ($Bmmb$) at 5GPa $\rightarrow$ cubic ($I2_1$3)at 215GPa [4]. It was also reported that insulating ground state phase of Li$_2$C$_2$ with the band gap of 3.7eV turns metallic in the $Bmmb$ phase, while $I2_1$3 phase is again insulating with a band gap of 2.7eV. This interesting shift in the band gap and electronic properties of Li$_2$C$_2$ in three phases perused us to investigate the optical properties of the same in the three phases which are not yet reported. Furthermore being high band gap insulator Li$_2$C$_2$ is predicted to have useful optical properties for potential applications in optoelectronic devices.

The present work is intended to investigate in detail the electronic and optical properties of Li$_2$C$_2$ in $Immm$, $Bmmb$ and $I2_1$3 phases using full potential linearized augmented plane wave method plus local orbitals (FP-LAPW+lo) method.

Computational Details

In order to investigate the structural, electronic and optical properties, the accurate FP-LAPW+lo method is used to solve Kohn–Sham equation within DFT [5] formulation as employed in the WIEN2k computer code [6]. The Engel-Voskogeneralized gradient approximation (EV GGA) [7] scheme is adopted to calculate the exchange-correlation energies. The charge density and potential were all expanded into two different basis sets. Inside the non-overlapping spheres surrounding the atomic sites (muffin-tin (MT) spheres), the potential was expanded into spherical harmonics with $l_{\text{max}} = 10$, while in the remaining (interstitial) regions the potential was expanded as plane waves. A plane wave cut off of $K_{\text{max}} = 7/R_{\text{MT}}$ was used for the expansion of the wave function inside the interstitial regions;
where \( R_{MT} \) is the average radius of the MT spheres and \( K_{\text{max}} \) is the maximum value of the wave vector \( K = k + G \).

### Results and Discussion

The band structure (BS) and density of states (DOS) of \( \text{Li}_2\text{C}_2 \) are calculated and shown in figures 1 and 2, respectively. It is clear from the DOS profile that the top of the valence band and the bottom of the conduction band for \( \text{Immm} \) phase have a major contribution from hybridizations of 'p' and 'd' states of both 'Li' and 'C' atoms. Clearly, an indirect band gap of 4eV along 'N' to 'Γ' direction can be seen from the band structure profile shown in Fig. 2(a) for \( \text{Immm} \) phase.

**Figure 1.** Total and partial DOS for \( \text{Li}_2\text{C}_2 \) for the three phases

**Figure 2.** Bandstructure of \( \text{Li}_2\text{C}_2 \) in (a) \( \text{Immm} \), (b) \( \text{Bmmb} \) and (c) phases

For \( \text{Bmmb} \) phase's' and 'p' orbitals of carbon forms three \( \sigma \) and one \( \pi \) band lying in the energy range from -14eV to -2.5eV. Furthermore, anti-bonding \( \pi \) band of carbon hybridizes with 's' and 'p' states of 'Li' and is dispersed from -1eV (below the Fermi-level) to 2eV (above the Fermi-level)is responsible for the metallic character of \( \text{Li}_2\text{C}_2 \) in \( \text{Immm} \) phase. The metallic character is due to \( sp^2 \) like hybrids in \( \text{Immm} \) phase. The cubic \( \text{I}_2\text{13} \) againacquires an insulating nature with a band gap of 2.9eV due to diamond like \( sp^3 \)hybridization. Our calculated bandgap values for \( \text{Li}_2\text{C}_2 \) for \( \text{Immm} \) and \( \text{I}_2\text{13} \) are in close agreement with earlier studies [4].

Optical properties are calculated in terms of dielectric function, reflectivity and optical conductivity. Dielectric functions of the ternary alloys are calculated using the following equations [8, 9].

\[
\varepsilon_2(\omega) = \frac{8}{2\pi \omega^2} \sum_{\sigma} \left| \sum_{n} P_{n\sigma}(k) \right|^2 \frac{dS_{\sigma}}{\omega S_{n\sigma}(k)},
\]

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

\(\varepsilon_{\text{el}}(k)\) is the dipole matrix elements between initial and final states, \( S_k \) is an energy surface with constant value, \( w_{\text{rel}}(k) \) is the energy difference between two states and \( p \) in Eq. 2, denotes the principal part of the integral.

The optical conductivity \( \sigma(\omega) \) and normal incident reflectivity \( R(\omega) \), are calculated using the following equations

\[
\sigma(\omega) = \frac{2W_{\text{ev}} \hbar \omega}{E_0},
\]

\[
R(\omega) = \frac{\pi - 1}{\pi + 1} = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}.
\]

Where, \( W_{\text{ev}} \) is transition probability per unit time.

Frequency dependent real and imaginary parts of the dielectric functions \( \varepsilon_1(\omega) \) & \( \varepsilon_2(\omega) \) of \( \text{Li}_2\text{C}_2 \) with electric field polarization along different crystallographic axis is shown in Fig.3. A considerable anisotropy in spectra of \( \varepsilon_1(\omega) \) & \( \varepsilon_2(\omega) \) for \( \text{Immm} \) and \( \text{Bmmb} \) is observed while \( \text{I}_2\text{13} \) being cubic phase show no anisotropy. For \( \text{Immm} \) phase real part of the dielectric function for all electric field polarizations starts with a value between 2 to 4 at zero frequency and remains smooth up to energy below 5eV and then shows abrupt peaks at around 5eV which is linked with the fundamental band gap. Furthermore, it can been seen that the relative optical anisotropy (i.e. the difference between values of \( \varepsilon_1(\omega) \) for \( \vec{E}/\vec{x}, \vec{E}/\vec{y} \) and \( \vec{E}/\vec{z} \) axis) increases with increase in energy. The dielectric function for \( \text{I}_2\text{13} \) remains high in the energy range 4 to 9eV. On the basis of a high dielectric coefficient in the high UV range this material is highly suitable for use in opto-electronic devices.
Reflectivity and optical conductivity of the compound in different phases is also studied. The reflectivity spectra are shown in Fig. 4. Reflectivity spectra of Li$_2$C$_2$ show different behaviour for Immm and I2$_1$ 3 phases i.e. the reflectivity is maximum at about 5eV for Immm phase and keeps on decreasing with increase in energy on the other hand reflectivity for I2$_1$ 3 phase is small at low energy, keep increasing and attains maximum value at 23eV energy. The optical conductivity spectra are shown in Fig. 5. Optical conductivity spectra of Li$_2$C$_2$ for Immm and I2$_1$ 3 phases remain high in the energy range 5 to 15 eV. It may further be noted that the relative anisotropy for reflectivity and optical conductivity spectra increase with energy.

Conclusions

In summary, electronic and optical properties of Li$_2$C$_2$ are calculated using FPLAPW within DFT. Immm and I2$_1$ 3 phases show insulating behaviour and Bmmb phase have metallic characteristics. The two phases Immm and I2$_1$ 3 show high dielectric function and optical conductivity in the high UV range and are therefore suitable to be used in the fabrication of optoelectronic devices.

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