Tuning the electronic and optical properties of the sphalerite by adsorbing halogen and alkali metals

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Abstract
The electronic and optical properties of sphalerite (ZnS) are modulated by adsorbing alkali metals (Li, Na, K, Rb, Cs) and halogen (F, Cl, Br, I, At). Simulations based on density-functional theory are used to study the electronic and optical properties of pristine sphalerite and alkali-halogen adsorbed sphalerite structures. The results suggest that pristine sphalerite has high absorption in several portions of ultraviolet (UV) region (λ < 250 nm) and negligible absorption in the visible and IR region. The alkali-halogen adsorbed structure of sphalerite results in red-shift phenomenon in which an increase in absorption coefficient with wavelength is observed or spectrum shifting towards the red end is observed. Strong absorption for both alkali and halogen adsorbed nano-structures is found throughout the visible zone (~410 to 780 nm) of the spectrum. Bromine adsorbed sphalerite structure results in highest value of absorption in visible region in comparison to other alkali and halogen adsorbed structures. This shift in absorption peaks from UV region to desired visible region range is beneficial for optoelectronic applications and in fabrication of optoelectronics devices such as LED, ARC, solar cells, CRTs and sensors.

1 | INTRODUCTION

Zinc sulphide (ZnS) is a wide bandgap direct transition II–VI semiconductor, an inorganic compound, which is non-toxic and abundantly available on Earth. [1]. ZnS has three polymorphs: sphalerite (cubic zinc blende), wurzite (hexagonal), and rarely observed cubic rock salt [2]. Both sphalerite and wurzite structures have tetrahedral bonding with a variation in the stacking order of atomic layers. Sphalerite is the main form of zinc sulphide found in nature. The most stable phase of ZnS is sphalerite in the bulk form at low temperature and ambient pressure. The sphalerite structure of ZnS transforms into a hexagonal wurzite structure at 1020°C. The high-temperature stable phase is the wurzite structure of ZnS, which melts at 1650°C [3, 4]. Both polymorphs of zinc sulphide have wide industrial applications. Zinc sulphide is a potentially suitable compound as an antireflection coating material for heterojunction solar cells [5]. ZnS is an important compound used in visible and near-ultraviolet light detection, emission, and modulation devices [6, 7].

The nanostructures of zinc sulphide have been used in solar energy exploitation, fuel cells, ARC, and non-linear optical devices. Aluminium-doped n-type ZnS nanowires have been suggested to be used in high-performance UV and humidity sensors in [8]. ZnS nanobelts have been suggested in [9, 10] for application in ultraviolet light emitters, sensors, and lasers. In [11], ZnS nanowire and nanoribbon arrays are reported for use in nanolasers and other photonic devices in UV and visible regions. ZnS is among the foremost compounds for electroluminescent thin-film displays [12] and blue light-emitting laser diodes [13]. Zinc sulphide’s phosphorescence property is used in infrared optical window, thin-film electroluminescence, and cathode ray tube [14, 15]. Although wurzite ZnS has better optical properties than sphalerite ZnS [16], synthesis of pristine wurzite ZnS nano-crystals is difficult at temperatures below 200°C [17].

ZnS has high absorption in the ultraviolet region and negligible absorption in the visible range [18]. It is therefore of interest to tune/shift the absorption of ZnS into the desired visible range so that it can be useful in solar cells and other...
optoelectronic devices fabrication. The electronic and optical properties of a ZnS nanostructure are not only varied and customisable with its size, shape, phase, doping, and adsorption of other materials, but also provide a foundation to construct future nano-scale devices through a self-assembled bottom-up approach [19, 20].

In the past, researchers showed a lot of interest in alkali-metal and halogen adsorbed semiconductors as fundamental building blocks for semiconductors with tuneable optical properties [21–34]. A semiconductor can behave as a n-type or p-type semiconductor, or semi-metallic by adsorbing alkali or halogen on it, which results in a decrease in its work function for the n-type and an increase in the case of the p-type. Optical properties also change along with the electronic properties on adsorbing alkali and halogens. Therefore, it would be interesting to investigate the impact of alkali and halogen adsorption on the optical properties of sphalerite. Herein, alkali and halogen type materials are adsorbed over sphalerite ZnS to investigate shifting/tuning of the optical absorption within the desired visible range (λ ≈ 410–780 nm).

2 | COMPUTATIONAL DETAILS

In order to obtain the optical and electronic properties of sphalerite adsorbed with halogen (F, Cl, Br, I, and At) and alkali metals (Li, Na, K, Rb, and Cs), self-consistent calculations using density functional theory (DFT) have been performed on an atomistic tool kit [35, 36]. The Perdew–Burke–Ernzerhof (PBE)-based generalised gradient approximation (GGA) exchange correlation [37, 38] is used on alkali-halogen adsorbed sphalerite structures in DFT calculations. The geometry-optimised structures are obtained by relaxing each structure using an LBFGS algorithm [39] with a force tolerance of ∼0.05 eV/Å. All calculations are performed using a double zeta polarised basis set.

The electronic and optical properties (electronic bandgap, absorption coefficient, dielectric constant, and refractive index) of optimised structures are calculated using DFT with meta-GGA approximation [40] and with grid mesh cut-off of 120 Ry. To study the optical spectrum, broadening has been set to 0.01 eV on account of the thermal effects on the structures with a k-point sampling of 10 × 10 × 10. The investigations into optical properties such as absorption coefficient, dielectric constant, and refractive index have been performed for pristine sphalerite and alkali-halogen adsorbed sphalerite.

To determine the susceptibility tensor, the Kubo–Greenwood formula [41] is used as:

\[
\chi_0(\omega) = -\frac{\varepsilon_0 \hbar^4}{\varepsilon_i m^2 \alpha} \sum_{m n} f(E_m) - f(E_n) \mathrm{Tr} \left( \frac{\pi_{nm} \pi_{mn}^i}{\hbar \omega - i \varepsilon_i} \right)
\]

where \( \pi_{mn}^i \) is the i-th element of the dipole matrix constituent within state m and n, \( \Gamma \) is the broadening, \( f \) is the Fermi function, and \( V \) is the volume.

The polarisability (\( \alpha \)) and the relative dielectric constant (\( \varepsilon_i \)) are correlated with the susceptibility as:

\[
\alpha(\omega) = V \varepsilon_0 \chi(\omega),
\]

\[
\varepsilon_i(\omega) = \left( 1 + \chi(\omega) \right),
\]

The expression for optical conductivity \( \sigma \) is [36]:

\[
\sigma(\omega) = -i\omega \varepsilon_0 \chi(\omega)
\]

The relative dielectric constant is the function of the extinction coefficient \( \kappa \) and the refractive index \( \eta \) as:

\[
\eta + i\kappa = \sqrt{\varepsilon_i}
\]

The extinction coefficient \( \kappa \) and the refractive index (\( \eta \)) are the function of the real \( (\varepsilon_1) \) and imaginary parts \( (\varepsilon_2) \) of the dielectric constants given as:

\[
\kappa = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1}{2}}
\]

\[
\eta = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_1}{2}}
\]

The optical absorption coefficient (\( \alpha_\omega \)) is associated with the extinction coefficient \( \kappa \) through [42], refractive index (\( \eta \)) and the imaginary parts \( (\varepsilon_2) \) of the dielectric constants as:

\[
\alpha_\omega = \frac{2\omega \varepsilon_2}{c}
\]

where \( \omega \) is frequency and \( c \) is speed of light.

3 | RESULTS AND DISCUSSION

Before calculating optical properties of all the structures shown in Figure 1 (relaxed), all the structures were relaxed using the LBFGS geometry optimisation method until all the residual forces on any atom were less than or equal to 0.05 eV/Å. The optimised structure bond lengths are given in Table 1.

The band structure of pristine sphalerite is shown in Figure 2. The Brillouin-zone integrations are carried out along Γ, A, C, B, Γ, Y, X, Z, L. For pristine sphalerite, the optical bandgap obtained is 3.8675 eV and the calculated binding energy is 32.5 meV, which is in confirmation with the previously reported works [43, 44]. A direct bandgap of ∼3.9 eV (see Figure 2) and exciton binding energy ∼34 meV are obtained for pristine sphalerite, which is also in confirmation with the results reported in [45].
The bandgap openings in alkali metals and halogen adsorbed sphalerite structures are negligibly small except the fluorine adsorbed structure exhibiting a direct bandgap opening of $\sim0.67$ eV.

To check the stability of alkali and halogen adsorbed structures, the authors calculated their binding energies defined by $E_B = (E_{\text{吸附}} - (E_{\text{ZnS}} + E_{\text{alkali/halogen}}))/N$, where $E_{\text{吸附}}$, $E_{\text{ZnS}}$ and $E_{\text{alkali/halogen}}$ represent the total energies of alkali-halogen adsorbed structure, pristine sphalerite, and alkali/halogen atoms, respectively, and the total number of atoms in the adsorbed structure is represented by $N$ [3]. The calculated binding energies of all except Rb and Cs adsorbed sphalerite structures are either negative or negligibly small, which indicates their favourable stabilisation. However, the binding energies of Rb and Cs adsorbed sphalerite structures are positive, indicating the least stable configurations.

The stability of ZnS nanostructures has also been reported by several other experimental and simulation studies. In [46], the stability of endohedrally doped ZnS clusters has been confirmed by ab initio simulations. In [47], a wet-chemical precipitation method is optimised for the synthesis of ZnS nanocrystals doped with Cu$^+$ and halogen. The nanoparticles were stabilised by capping with polyvinyl pyrrolidone (PVP). When the sizes of the ZnS nanostructures reduce to just a few nanometres, the high-temperature WZ structure becomes stabilised, as shown in [48]. ZnS nanocrystals with high colloidal stability in aqueous and methanol media using Na$_2$S and Zn(ClO$_4$)$_2$ as precursors are synthesised in [49]. In an experimental study on BN-coated ZnS [50], it has been shown that ZnS/BN core–shell nanoarchitectures have excellent stability. In another experimental study [51], it has been shown that ZnS nanocrystals prepared in polymer matrices possess good stability. Few other experimental studies have also demonstrated stability of ZnS nanomaterial, as in [52–55].

The dielectric constant explains how incident light interacts and propagates through the structure. The amorphous dispersion and polarisation effects are described by the real part, while measurement of energy retention in a structure as an outcome of neutral charge excitations is delineated by the imaginary portion of its dielectric constant.

The real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) components of the energy-dependent dielectric function are calculated for all configurations (see Figures 3 and 4) with respect to $xx$, $yy$, and $zz$ tensors. The polarisation of the electric field parallel to the surface is only considered in the calculations, hence only $xx$ components of the optical constants are estimated [56]. The imaginary part ($\varepsilon_2$) is a key parameter to investigate the optical absorption in compounds, hence the curves of the imaginary part along the $xx$ direction are considered explicitly and the results in the other two directions can be concluded in a similar way [57].

The imaginary portion of the dielectric constant spectrum within the photon energy range 0–5 eV is shown in Figure 4. For the pristine sphalerite, the loss factor remains constant and negligibly small with an increase in photon energy within the energy range 0–3.8 eV, after which it increases as the imaginary dielectric constant also increases in this energy range with an increase in photon energy in the range 3.8–5 eV. For all alkali and halogen adsorbed sphalerite structures (except rubidium and fluorine) in Figure 4, a significant peak in imaginary dielectric constant is seen in the photon energy range 0–0.5 eV followed by a sharp decay with any further increase in photon energy. The peaks in the imaginary dielectric function within
the energy range 0–0.5 eV suggest a smaller exciton binding energy of the system in this energy range, consequently resulting in a sharp increase in the photon absorption in this energy range (see Figure 5). The optical absorption depends on the interband electronic transitions. Due to the photon-electron interaction, the electronic interband transition takes place in a semiconductor between occupied and unoccupied states. The absorption coefficient is a function of dielectric coefficient and photon energy. The semiconductors that have high absorption coefficient have high absorption of photons, which triggers electrons in the conduction band.

To calculate the absorption index, Equation (8) was used for all structures shown in Figure 5. The absorption coefficient of pristine sphalerite is constant within the energy range 0–3.75 eV, and it then increases with an increase in photon energy in the range 3.75–5 eV, as shown in Figure 5. The optical absorption spectra for sphalerite structures adsorbed with Li, Na, K, F, and Br show a right (red) shifting of the peaks of the absorption coefficient towards visible and IR regions. The absorption peak is spread across the visible region and UV region in Rb, Cs, Cl, I, and At adsorbed sphalerite structures. The Br adsorbed structure results in maximum absorption in the visible region, in comparison to all alkali and halogen adsorbed structures considered herein. The dielectric constant (ε2) peaks (see Figure 4) for all structures considered here are strongly correlated to their bandgaps (see Figure 2). The absorption edges shift towards a lower energy range on adsorption of alkali and halogen on sphalerite. The presence of a red shift phenomenon is detected by observing the absorption edges in the adsorbed sphalerite structure, resulting in stable and high absorption within the visible range in comparison with its constituent crystals. Thus, the adsorbed sphalerite shows enhanced absorption for the visible light region. The spectrum range and absorption rate of the adsorbed sphalerite are much larger than its constituent pristine sphalerite in the desired visible region of the spectrum, which makes them more suitable for optoelectronic applications. Furthermore, the xx and yy tensors in pristine sphalerite almost overlap each other, with zz being separate. This confirms the isotropic/anisotropic property of monolayer pristine sphalerite [58]. Similarly, observing for the adsorbed sphalerite, anisotropy behaviour is observed as seen in Figures 3–6.

The refractive index (n) of the semiconductors is the function of dielectric constants (ε1, ε2) as given in Equation (6). For all the structures (shown in Figure 6), the refractive index is calculated along xx, yy, and zz tensors along with the photon energy. The refractive index for pristine sphalerite slightly increases in the energy range 0.4–5 eV. The static refractive index is the highest peak for all adsorbed structures and it decreases with the photon energy. This decay in the refractive index with photon energy indicates normal dispersion behaviour of the adsorbed sphalerite structures. The peaks in refractive index (see Figure 6) are consistent with the trends in dielectric constant (see Figures 3 and 4), thereby confirming that the refractive index is also following the trends in dielectric constant and absorption coefficient. The spectrum range in which an increase in refractive index is observed suggests high absorption due to the light being trapped for a much longer duration in that range, resulting in a larger photon absorption within the range. Similarly, lower absorption would result in regions with lower refractive index, which is consistent with the dielectric function dielectric function (ε2).

### Table 1: Calculated average bond lengths of pristine and adsorbed sphalerite

| Configuration                  | Average bond length (Å) with Zn | Average bond length (Å) with S |
|-------------------------------|---------------------------------|--------------------------------|
| Pristine sphalerite           | 2.3423                          | 2.3423                          |
| Lithium adsorbed sphalerite   | –                               | –                              |
| Sodium adsorbed sphalerite    | 2.5727                          | –                              |
| Potassium adsorbed sphalerite | 2.3054                          | –                              |
| Rubidium adsorbed sphalerite  | 2.3280                          | 2.7194                          |
| Caesium adsorbed sphalerite   | 2.7049                          | –                              |
| Fluorine adsorbed sphalerite  | 2.0317                          | –                              |
| Chlorine adsorbed sphalerite  | 2.3041                          | –                              |
| Bromine adsorbed sphalerite   | 2.3523                          | –                              |
| Iodine adsorbed sphalerite    | 2.4036                          | –                              |
| Astatine adsorbed sphalerite  | 2.3362                          | 2.2379                          |

**Figure 2** The calculated pristine sphalerite band structures.
4 | CONCLUSION

In conclusion, first-principles calculations of the density-functional theory are used to investigate the optical properties of a pristine sphalerite structure and compared with halogen and alkali adsorbed sphalerite structures. The results suggest that pristine sphalerite has a direct bandgap of 3.9 eV and adsorbed sphalerite structures have negligible
bandgap, except for fluorine with a bandgap of ~0.67 eV. The optical properties of pristine sphalerite are suggested to be tuned by adsorbing alkali and halogen atoms. The alkali and halogen adsorbed sphalerite structures show that the absorption coefficient peaks spread and shift into the visible and IR region, with Br adsorbed structure resulting in maximum absorption in the visible region. This shift is important for finding the use of sphalerite ZnS in optoelectronic applications and other solar energy-harvesting applications.
FIGURE 5 Absorption coefficient: (a) pristine sphalerite; (b) lithium adsorbed sphalerite; (c) sodium adsorbed sphalerite; (d) potassium adsorbed sphalerite; (e) rubidium adsorbed sphalerite; (f) caesium adsorbed sphalerite; (g) fluorine adsorbed sphalerite; (h) chlorine adsorbed sphalerite; (i) bromine adsorbed sphalerite; (j) iodine adsorbed sphalerite; (k) astatine adsorbed sphalerite
FIGURE 5 (Continued)
**FIGURE 6** Refractive index: (a) pristine sphalerite; (b) lithium adsorbed sphalerite; (c) sodium adsorbed sphalerite; (d) potassium adsorbed sphalerite; (e) rubidium adsorbed sphalerite; (f) caesium adsorbed sphalerite; (g) fluorine adsorbed sphalerite; (h) chlorine adsorbed sphalerite; (i) bromine adsorbed sphalerite; (j) iodine adsorbed sphalerite; (k) astatine adsorbed sphalerite.
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