Ab initio study of structural, electronic and elastic properties of CdSe$_{1-x}$S$_x$ semiconductor

Muhammad Zafar[a,*], M. Shakil[b], Shabbir Ahmed[a], Muhammad Raza-ur-rehman Hashmi[a], M.A. Choudhary[a], Naeem-ur-Rehman[c]

[a] Simulation Laboratory, Department of Physics, The Islamia University of Bahawalpur, 63100, Pakistan
[b] Department of Physics, University of Gujrat, Gujrat 50700, Pakistan
[c] Department of Basic Sciences and Humanities, Khwaja Fareed University of Engineering & Information Technology, Rahim Yar Khan, Pakistan

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ABSTRACT

In this work plane wave pseudo-potential method was used to study the structural, electronic, and elastic properties of zinc-blende CdSe$_{1-x}$S$_x$ semiconductor alloys using local density approximation (LDA). The ground-state properties are resolute for the bulk materials CdS, CdSe, and their alloys. Very small deviation of the lattice constant from Vegard's law was observed for CdSe$_{1-x}$S$_x$ alloys at different concentrations but a little larger deviation of the bulk modulus from linear concentration dependence (LCD) was observed for considered alloy with downward bowing. We have also explored the effect of Sulfur composition on electronic properties using LDA and LDA + U. It was observed that by applying LDA + U method band gap for CdSe$_{1-x}$S$_x$ enhanced to experimental value. Elastic constants such as C$_{11}$, C$_{12}$, C$_{44}$, Young Modulus, and Shear Modulus are also calculated and it is observed that CdSe$_{1-x}$S$_x$ compound is ductile in nature.

1. Introduction

The zinc (Zn), cadmium (Cd) and mercury (Hg) oxides and chalcogenides are considered promising materials for applications in Gamma-rays detectors, solar cell's infrared windows (Wei and Zhang, 2000), opto-electronic devices such as LEDs, lasers, sensors, and solar cells as c-Si (Budiman et al., 2014). Easy and simple techniques of synthesis, direct and wide range of energy gaps and doping flexibility for both types (*i.e.* n and p) make them attractive candidates for optoelectronic industry. These II–VI materials are being studied extensively during last few decades due to their interesting technological activities (Yadav et al., 2010). It is well known that, CdS and CdSe exist in both wurtzite (Murali and Jayasuthaa, 2009; Yadav et al., 2010) and metastable zinc-blende (ZB) structures under normal conditions (Madelung et al., 1982; Mujica et al., 2003). Similarly, size-dependent tunability makes such materials ideal to use in photo-voltaics, LEDs and biological labeling. In particular, the compositional range of band gap energies for this alloy lies between UV and visible spectrum. This range of band gap makes it potentially important material for biological imaging applications, where nano-crystals of the same size but with varying optical properties might be advantageous. Lindsay and Nima reviewed the effect of grapheme and carbon nano tubes as a buffer layer with front and back contacts in thin film solar cells based on CdTe and

Cu(In,Ga)(S,Se) materials (Kuhn and Gorji, 2016). They also modeled the perovskite and thin film solar cells which were fitted to various CdTe, CIGS, CZTS materials successfully (Darvishzadeh et al., 2017).

In order to develop and design highly efficient devices based on these materials, it is envisaged that the full spectrum of band gap energies can be realized through systematic replacement of Se by S in CdSe, which result in a gradual modified physical properties. This modification can be attributed to the small difference in elector-negativities as well as sizes of S and Se. To achieve more meaningful theoretical band gaps for CdSe$_{1-x}$S$_x$ in the zinc-blende phase, closer to the experimental one, LDA + U approach was implemented. By using this approach the band gap of the alloy increases to experimental band gap and hence the LDA + U technique is better than LDA to calculate the band gap. The motivation behind the present study was to analyze the physical properties of CdSe$_{1-x}$S$_x$ for its possible applications in photonic devices operating in visible to UV spectral region. The elastic constants are important and vital parameters to describe the response to an applied macroscopic stress and especially they are important as they relate the various physical properties, such as the elasticity, mechanical stability and stiffness of materials. The obtained results are arranged as: Section 1 contains a brief introduction. In Section 2 we described the computational technique adopted for the calculations. Results and discussions are described in Section 3. Finally, the conclusions drawn are presented in Section 4.

* Corresponding author.
 E-mail address: zafartariq2003@yahoo.com (M. Zafar).

Table 1
Comparison of calculated lattice parameters (a_0) and bulk moduli (B) of $CdSe_{1-x}S_x$ alloys with experimental and theoretical results in ZB structure.

Compositions X	Lattice constant a_0 results (Å)			Bulk modulus B (GPa)		
	This work Å	Expt. Å	Other calculations	This work	Expt.	Other calculations
0.00	6.0217	6.05[a]	6.216[b] 6.055[c] 6.065[d] 6.10[e]	56.7	53[a]	45.16[b] 54.6[c] 55.05[d] 64.62[e]
0.25	5.9679		5.887[d] 6.05[e]	57.2		57.27[d] 49.45[e]
0.50	5.9092		5.952[d] 5.99[e]	58.8		59.05[d] 54.30[e]
0.75	5.8117		5.887[d] 5.92[e]	64.1		60.82[d] 57.31[e]
1.00	5.7589	5.82[a]	5.95[b] 5.815[c] 5.807[d] 5.83[e]	67.1	62[a]	56.84[b] 62.3[c] 64.04[d] 72.27[e]

[a] Madelung et al. (1982).
[b] Ouendadji et al. (2010).
[c] Guo et al. (2013).
[d] Ameri et al. (2014).
[e] Khan et al. (2013).

2. Computational details

DFT based software, Quantum ESPRESSO, was used to calculate structural, electronic, and elastic properties of $CdSe_{1-x}S_x$ alloys (Paolo, 2009). In this code pseudo potential method has been used to solve the Kohn Sham (K-S) equations. It yields well consistent results for the physical properties of numerous solids. Local density approximation (LDA) proposed by Perdew and Zunger (Perdew and Zunger, 1981)is used to calculate the physical properties of $CdSe_{1-x}S_x$. Plane waves with 30 Ry, cutoff energy, were used to represent the electronic wave functions. Integrations of Brillion zones were carried out by $8 \times 8 \times 8$ Monkhorst-Pack (Monkhorst and Pack, 1976) grid of k-point mesh. Standard procedure was used for the calculation of the ground state lattice constants, and bulk modulli *i.e.* by calculating the total energy at different lattice constants and fitting the Murnaghan's equation of states (Murnaghan, 1944). As LDA and GGA both calculate very small energy gap so a Hubbard U correction (Anisimov et al., 1991) was used along with LDA for the correction of electronic band structure of $CdSe_{1-x}S_x$. Elastic constants and moduli were calculated by Lagrangian theory of elasticity (Wallace, 1998).

3. Structural properties

Ground state structural parameters of pure CdS and CdSe and their ternary alloys were calculated by fitting total energy verses different lattice constants.

Alloys were modeled at some selective Sulfur defects with ordered structures described in terms of periodically repeated super-cells containing eight atoms at x = 0.25,0.5, and 0.75. The obtained values are fitted with the Murnaghan equation of state.

$$E(V) = E_0 + V\left(\frac{B}{B'}\right)\left[\left(\frac{V_0}{V}\right)^{\frac{B'}{B'-1}} + 1\right] - \frac{BV_0}{B'-1} \tag{1}$$

And corresponding pressure $P = -dE(V)/dV$ is

$$P(V) = \left(\frac{B}{B'}\right)\left[\left(\frac{V_0}{V}\right)^{B'} - 1\right] \tag{2}$$

Here E_0 (minimum energy), V_0 (equilibrium volume), B (Bulk modulus) and B' (pressure derivative of B) are fitting parameters. Ground state structural parameters such as a_0 (lattice constants) and B_0 (bulk modulus) were obtained for both binary and their tertiary alloys and are given in Table 1 and plotted in Fig. 2. It was considered that GGA usually over estimates (Mokhtari and Akbarzadeh, 2002) and LDA underestimates the lattice parameters. Obtained results of this study are in well agreement with previous experimental and theoretical studies. The results reflect that the lattice constants of studied alloy decreases linearly with the addition of Sulfur in CdSe. The inverse of the bulk modulus is called the compressibility. The order of compressibility from high to low is CdSe (56.7 GaP) > $CdSe_{0.75}S_{0.25}$ (57.2 GaP) > $CdSe_{0.50}S_{0.50}$ (58.8 GaP) > $CdSe_{0.25}S_{0.75}$ (64.1 GaP) > CdS (67.1 GaP). This decrease in compressibility may be due to the smaller atomic mass of Sulfur as compared to Selinium. Since Bulk modulus and compressibility are inverse to each other. So, for these periodic structures, CdSe has the largest bulk modulus (67.1 GaP), thus it may be a less compressible compound with smaller compressibility than CdS.

Usually, by the so-called Vegard's law to treat the alloys, it is supposed that the atoms are situated at the perfect lattice sites and a_0 changes linearly by the addition of composition x. (Vegard, 1921):

$$a(AB_{1-x}C_x) = xa_{AC} + (1-x)a_{AB} \tag{3}$$

In Eq. (3) 'a_{AC}' and 'a_{BC}' represents lattice constants of the binary compound AC (CdS) and AB (CdSe) respectively and ($AB_{1-x}C_x$) are the lattice constants of alloys. However, for semiconductor alloys deviation in a_0 and B has been observed from Vegard's law both experimentally (Jobst et al., 1996) and theoretically (Dridi et al., 2005). Hence, the equation can be stated as:

$$a(AB_{1-x}C_x) = xa_{AC} + (1-x)a_{AB} - x(1-x)b \tag{4}$$

In the above quadratic Eq. (4) the term 'b' represents bowing parameter. Figs. 1 and 2, showed the calculated a_0 and B for $CdSe_{1-x}S_x$ (x = 0–1) along with Vegard's law. This law demands that the lattice constants of alloys must vary linearly with the change in composition x (Vegard, 1921). Our computed lattice constants at different x were found to be varying linearly in downward direction. Hence this linearity validates the Vegard's law for our simulated results.

4. Electronic properties

Band structure and band gaps of pure CdS, CdSe, and their ternary alloys are calculated using LDA and LDA+U (U = 6.0 eV) at high symmetry points for the investigation of electronic properties. High symmetry points were considered in first Brillion zone for the cubic structure.

Both valence band maxima (VBM) and the conduction band minima (CBM) arise at the Γ point; that revealed all compounds are direct band gap semiconductors. A prominent increase in band gap was found from CdSe (1.8845 eV) to CdS (2.528 eV) and this increasing behavior can be observed from Table 2 and Fig. 3.During the de-excitation process DBG semiconductors have fast decay time specialty over indirect band gap (IBG) materials. This specialty is important for the optically active materials in opto-electronic devices, and thus $CdSe_{1-x}S_x$ alloys are considered to be optically active in the visible range. For better understanding the variation in energy gap by replacing the Selenium with Sulfur, the change in gap verses composition x for the $CdSe_{1-x}S_x$ alloy is shown in Fig. 4(a)–(e). The outcomes are listed in the Table 3 to compare them with experimental and other values, and it is found that band gap values are comparable with the experimental ones.

4.1. Densities of states

Density of States (DOS) infer about bonding nature and the location of different energy orbitals in materials. It also helps to explain the character of different band states of various materials. In Fig. 5, we present the partial density of states (PDOS) paired with total densities of