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First-principles study on crystal structures and bulk modulus of $CuInX_2$ (X = S, Se, S-Se) solar cell absorber

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Abstract. Chalcopyrite semiconductors are widely used as absorbers in thin film solar cells, especially flexible solar cells, due to their high power conversion efficiency. They also have interesting mechanical properties, making them promising materials for flexible, light, and thin solar cells. In this work, we report the first-principle calculations of the lattice constant and bulk modulus for $CuInS_2$, $CuInSe_2$, and $CuIn(S,Se)_2$ absorber solar materials. All calculations are performed using plane wave as implemented in the Quantum ESPRESSO software package in the framework of density functional theory using PBE-GGA approximations and ultrasoft pseudopotentials. The calculated lattice constant correlates well with the available experimental study. The energy-volume and pressure-volume relations are described using the third order of Birch-Murnaghan's equation of state to calculate the bulk modulus of the absorber solar material, which is associated to the hardness of a material under particular conditions. The values of bulk modulus obtained for $CuInS_2$ and $CuInSe_2$ are in good agreement with available theoretical results, except for $CuIn(S,Se)_2$, which have been calculated and reported for the first time.

1. Introduction

Metal chalcogenide semiconductors are currently interesting technologies due to their excellent physical and chemical properties, especially in the fields of electronic, optoelectronic, photonic, non-linear optic, and photovoltaic applications. Nowadays, there is strong demand for renewable energy as a result of the limited availability of non-renewable energy sources such as fossil and nuclear fuels, which has led to massive concerns regarding environmental and sustainability issues. The performance of solar cells has made it one of the potential alternatives for non-renewable energy resources, and it

has been the subject of intensive research, resulting in high power conversion and low environmental impact [1]. Currently, the solar technology is dominating by crystalline silicon (c-Si) panels with a global market share of about 80% [2]–[4]. However, conventional solar panels in the market are thick, heavy, and flat due to the structural components necessary to support the fragile and brittle c-Si solar cells [4]. To overcome the current limitations of c-Si solar panel, the thin film solar modules are introduced, which are less expensive to manufacture, lightweight, and flexible than traditional silicon-based panels [5]. To date, the world records for photovoltaic efficiency for thin film technologies based on metal chalcogenide compounds were obtained by Solar Frontier and First Solar for $Cu(In,Ga)Se_2$ and CdTe with 23.4% [6] and 22.1% [7] efficiency, respectively.

Ternary metal chalcogenide compounds with tetragonal chalcopyrite structure of $CuInS_2$ and $CuInSe_2$ have been widely used as absorbers in thin film solar cells due to their high absorption coefficient of about 10^5 cm^{-1} in the visible spectral range and adjustable bandgap with high thermal and chemical stability, which allows the utilization of low absorber thicknesses [8]–[11]. The stability, thermodynamic, optical, and electrical characteristics of these chalcopyrite semiconductors have attracted the attention of numerous researchers. Matter of fact, a number of scientists have published extensive experimental and theoretical work devoted to the features of these chalcopyrite semiconductors [12]–[14]. In addition, the elastic constant of chalcopyrite compounds is also vital to investigate in order to have a better knowledge of their mechanical characteristics. For example, Kumar et al. [15] have successfully investigated the structural and elastic properties of $A^{I}B^{III}C_2^{VI}$ groups such as $CuInS_2$ and $CuInSe_2$ using the density functional theory. Moreover, Amudhavalli et al. [16] investigated the elastic properties of several compound combinations of $A^{I}B^{III}C_2^{VI}$ groups such as $CuInS_2$ and $CuInSe_2$. On the other hand, there has not been much study reported on the elastic properties of $CuIn(S,Se)_2$ compounds. In this work, we investigated the structural and bulk modulus properties of the $CuInS_2$ (referred to hereafter as CIS), $CuInSe_2$ (referred to hereafter as CISe) and $CuIn(S,Se)_2$ (referred to hereafter as CISSe) absorber solar materials by using first-principle calculation based on the density functional theory framework.

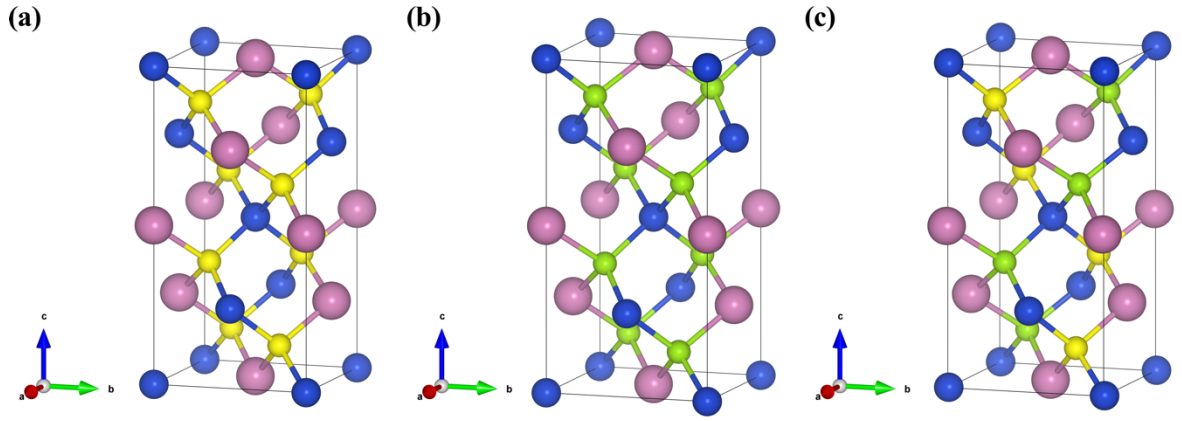

Figure 1. Chalcopyrite structure of unit cell of (a) CIS, (b) CISe, and (c) CISSe absorber solar cells. The blue, light magenta, yellow, and green spheres represent Ti, In, S, and Se atoms, respectively.

2. Computational Method

The first-principles calculations used to calculate the structural and bulk modulus were performed based on the DFT framework as implemented in the Quantum ESPRESSO (QE) code [17]. The exchange and correlation effects have been treated within Generalized Gradient approximations (GGA) with Perdew-Burke-Ernzerhof (PBE) [18] exchange correlation and the ionic potentials are described by ultrasoft pseudopotential (USPP) [19] wave which available from QE website. The electronic configuration of USPP for Cu, In, S, and Se were treated as valence electrons of Cu ($3d^{10}4s^1$) In ($4d^{10}5s^25p^1$), S ($3s^23p^4$), and Se ($3d^{10}4s^24p^4$) respectively. For the plane-wave basis, the

energy cut-off was fixed at 40 Ry. All the atoms were fully relaxed with maximum forces set at 10^{-5} Ry/Bohr. The errors on the total energy are set at 10^{-4} Ry/atom. The Brillouin-zone (BZ) were carried out using Γ-centered Monkhorst-Pack grids of $4 \times 4 \times 2$ k-points for ionic relaxations and self-consistent field (SCF) calculations. The tetragonal chalcopyrite structure with 16 atoms has been used to model the unit cell of CIS, CISe, and CISSe, as shown in Figure 1. The bulk modulus and its derivative were obtained by fitting the third order of Birch-Murnaghan equation of state (EOS) on calculated energy-volume and pressure-volume data.

3. Results and Discussion

In the first step, we constructed the tetragonal chalcopyrite of CIS, CISe, and CISSe as shown in Figure 1, and its geometrical structure were fully relaxed by PBE-GGA approximations and USPP pseudopotential. The computed optimized lattice parameters are tabulated in Table 1 and is comparable with the available reported experimental work. By comparing the calculated unit volume to the experimental value, the relative error is about 3.2% for CIS, 1.1% for CISe, and 0.8% for CISSe, with the CIS unit volume having the smallest relative deviation. The smallest values of relative deviation between present theoretical values and previous experimental work indicate that the fully relaxation by PBE-GGA-USPP have good lattice constant prediction.

Table 1. Computed lattice parameter and volume for optimized geometrical structure of CIS, CISe, and CISSe absorber solar cells.

Absorber Materials	Lattice Parameter			Experimental			
	a (Å)	*c* (Å)	V (Å^3)	*a* (Å)	*c* (Å)	V (Å^3)	ref
CIS	5.574	11.248	349.469	5.517	11.122	338.524	[20]
CISe	5.817	11.743	397.354	5.814	11.630	393.124	[21]
CISSe	5.719	11.512	376.523	5.700	11.500	373.635	[22]

The calculated bond length for optimized structure of CIS, CISe, and CISSe is tabulated in Table 2. The computed bond lengths of Cu-S and In-S in CIS are 2.327 and 2.523, Cu-Se and In-Se in CISSe are 2.422 and 2.640, and Cu-S, Cu-Se, In-S, and In-Se in CISSe are 2.299, 2.469, 2.539, and 2.638, respectively. The bond length of Cu-S and In-Se in CISSe has decreased compared to CIS and CISe, while the bond length of In-S and Cu-Se in CISSe has increased compared to CIS and CISe. Compared to the experimental value, the relative errors between the computed bond length and experimental values are about 1.70% (Cu-S) and 0.24% (In-S) for CIS, 0.49% (Cu-Se) and 1.97% (In-Se) for CISe, and there is no available bond length reported for CISSe.

Table 2. Computed bond length for optimized geometrical structure of CIS, CISe, and CISSe absorber solar cells, and available previous experimental data.

Absorber Materials	Bond Length (Å)				Experimental (Å)				
	Cu-S	In-S	Cu-Se	In-Se	Cu-S	In-S	Cu-Se	In-Se	Ref
CIS	2.327	2.523	-	-	2.288	2.517	-	-	[23]
CISe	-	-	2.422	2.640	-	-	2.434	2.589	[24]
CISSe	2.299	2.539	2.469	2.638	-	-	-	-	-

In the next step, third order of Birch-Murnaghan's EOS has been used to obtain bulk modulus and its first derivatives by fitting the calculated energy as a function of cell volume at 0 GPa pressure and 0 K temperature. The cell volume based on the fully relaxation calculations are varied by scale factor

of 0.93 to 1.05 with the interval of 0.01, and their ground state energy are calculated and plotted in Figure 2. The bulk modulus is obtained by extract the fits of Birch-Murnaghan EOS as follows.

$$E(V) = E_0 + \frac{9V_0B_0}{16}\left\{\left[\left(\frac{V_0}{V}\right)^{2/3}\right]^3 B_0' + \left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]^2\left[6 - 4\left(\frac{V_0}{V}\right)^{2/3}\right]\right\} \quad (1)$$

Where B_0, B_0', V_0, and E_0 are the bulk modulus, bulk modulus first derivative, unit cell volume and energy at equilibrium ground states, respectively. The calculated bulk modulus and its first derivative (in bracket) for CIS, CISe, and CISSe are 65.8 (4.80) GPa, 54.56 (4.89) GPa, and 60.00 (4.85) GPa, respectively, as tabulated in Table 3. It can be seen that the calculated bulk modulus is in close agreement with previous experimental work by less than 1.80 % error, which reveals the reliability of our calculations. The chi-square values obtained for CIS, CISe, and CISSe were 6.52×10^{-10}, 4.90×10^{-10}, and 4.62×10^{-10}. Figure 3 show the pressure evolution of the unit cell volume of (a) CIS, (b) CISe, and (c) CISSe obtained from our DFT calculations and fits of third order Birch-Murnaghan EOS. Our computation suggest a less dense state is less compressible when fitted to a third order Birch-Murnaghan EOS. The chi-square values obtained for CIS, CISe, and CISSe were 6.52×10^{-10}, 4.90×10^{-10}, and 4.62×10^{-10}.

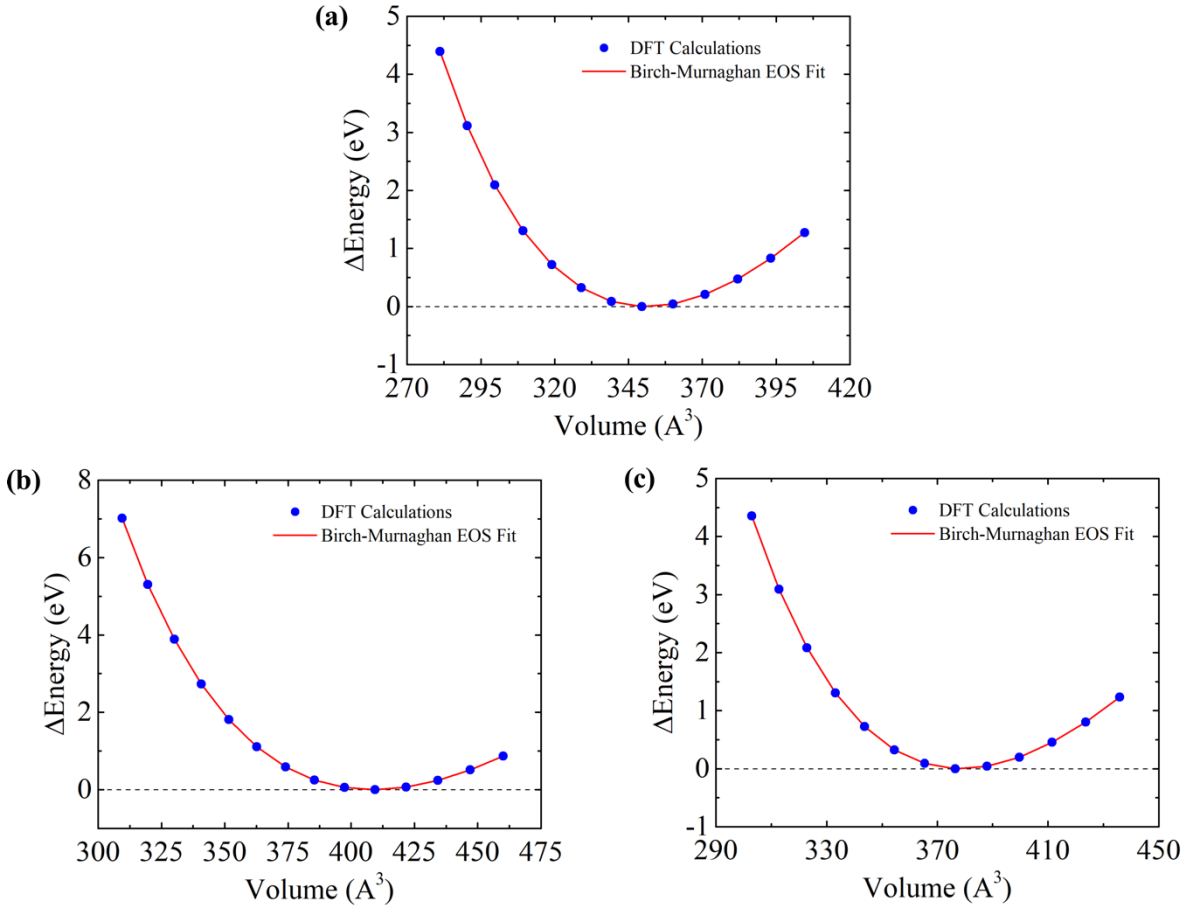

Figure 2. Energy-volume curves of calculated DFT data and fits of third-order Birch-Murnaghan EOS of (a) CIS, (b) CISe, and (c) CISSe absorber solar cells. Blue dots indicate calculated DFT values, while smooth red line is fitting of Birch-Murnaghan EOS.

Table 3. Extracted bulk modulus (B_0) and its first derivative (B_0') using Birch-Murnaghan EOS for CIS, CISe, and CISSe absorber solar materials with available previous theoretical works.

Absorber Materials		This Work	Other Theoretical Works
CIS	B_0 (GPa)	65.81	65.55 [25], 65.81 [26]
	B_0'	4.80	-
CISe	B_0 (GPa)	54.56	53.6 [27], 54.20 [25]
	B_0'	4.89	-
CISSe	B_0 (GPa)	60.00	-
	B_0'	4.85	-

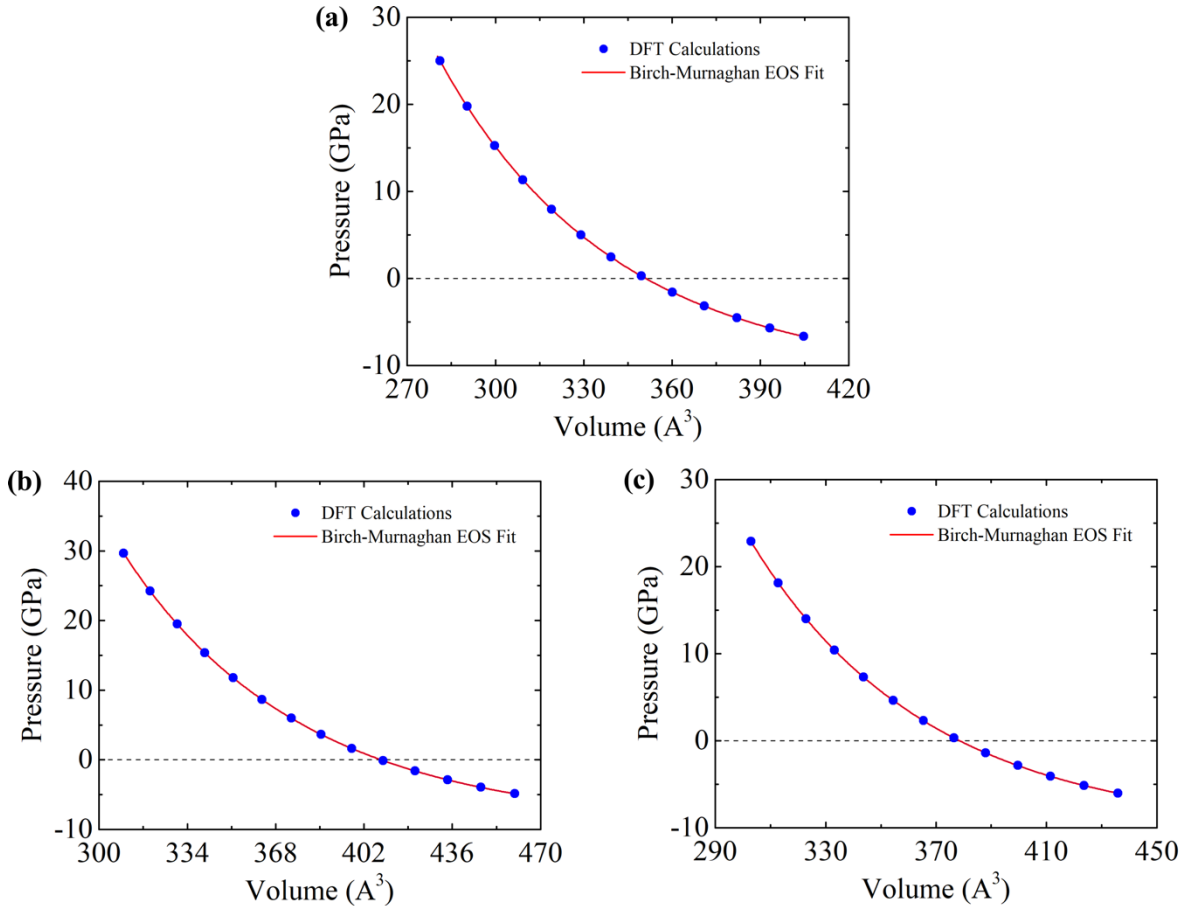

Figure 3. Pressure-volume curves of calculated DFT data and fits of third-order Birch-Murnaghan EOS of (a) CIS, (b) CISe, and (c) CISSe absorber solar cells. Blue dots indicate calculated DFT values, while smooth red line is fitting of Birch-Murnaghan EOS.

4. Conclusion

In summary, we have investigated the structural and bulk modulus of the CIS, CISe, and CISSe by employing the plane wave with PBE-GGA and USPP, which is based on DFT first principle calculation as implemented in Quantum ESPRESSO code. The lattice parameter and bulk modulus of all compounds were determined and compared. The results obtained show that the lattice parameters of CIS, CISe, and CISSe calculated using PBE-GGA and USPP successfully predict the crystal structure correctly and in good agreement with previous experimental results. The theoretical bulk modulus of the current work for CIS and CISe is found to be consistent with earlier theoretical values, and CISSe is theoretically reported for the first time.

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