First principles study of structural, electronic and elastic properties of hexagonal copper (I) selenide (Cu_2Se)

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Abstract. The first principle calculations within density functional theory, were used to explore the structural, electronic and elastic properties of hexagonal copper (I) selenide (Cu_2Se) at room temperature. Lattice constants, minimum energy and equilibrium volume at hexagonal phase were calculated. The lattice parameters of hexagonal Cu_2Se were found to be $a = b = 8.37$ *bohr (4.43 Å)* and $c = 9.94$ *bohr (5.26 Å)*, corresponding to the minimum energy of -1.15×10^4 *eV* with the equilibrium volume of 594.93 *bohr*^{3}. The electronic properties suggest a metallic behaviour with a zero band gap. Calculated elastic constants satisfy all the stability criteria's of a hexagonal system. The value (118.3 GPa) of Young's modulus shows that the material is malleable and ductile material. Elastic mechanical behaviour of hexagonal Cu_2Se, suggest stiff, ductile, incompressible, anisotropy and ionic bonding with shear to bulk moduli ratios of 0.38. Furthermore, elastic properties suggest possible consideration of hexagonal Cu_2Se for device fabrication in solar cells.

1 Introduction

Copper selenide (Cu_2Se) is an inorganic binary compound which is formed through the chemical reaction of copper metal and selenium non-metal. It can undergo oxidation, forming copper ions (Cu^{2+}) and selenide ions (Se^{2-}), and can also participate in solid-state reactions, such as cation exchange [1]. This binary compound can manifest in different chemical formulas but mostly in CuSe and Cu_2Se [2]. As a crystallographic compound, depending on temperature range, either CuSe or Cu_2Se may assume different crystal forms ranging from cubic to hexagonal with interesting semiconducting characteristics. A Cu_2Se polymorph is composed of relatively abundant and non-toxic elements, making it cost-effective and environmentally friendly [3]. Both CuSe and Cu_2Se polymorph-semiconductors have electronic, optical, and elastic properties suitable for photo-voltaic, thermoelectric devices and electro-catalytic applications [2].

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At ambient conditions, Gosayi et al. [4] stated that CuSe polymorph assumes a hexagonal phase, which transforms to orthorhombic form above 321 K. Furthermore**,** above 393 K, the orthorhombic CuSe transforms back to a hexagonal CuSe crystal [4]. Liu et al. [5] further reported that at room temperature, α-Cu_2Se conforms to a monoclinic crystal form, which transforms to a cubic β-Cu_2Se phase around 400 K. Throughout this phase transformation, a fluidic cloud of Cu^{1+} ions becomes kinetically disordered within the basal framework of face-centred cubic Se^{2-} ions. A combination of various factors needs to be considered in order to reach mechanical stability of copper selenides; crystal lattice structure, ionic and thermal conductivity, as well as availability of defects in the material [6]. Specifically, the ability to modulate copper ion mobility and introduce defects like Cu vacancies can enhance both thermoelectric performance and mechanical robustness [6]. However, the mechanical properties can vary depending on the phase, purity, and synthesis method [7]. Another fact, mechanical properties of copper selenide may change with the changing temperature. Hasan et al. [8] calculated mechanical properties of the cubic Cu_2Se crystals using the density functional theory method. Calculated elastic constants, provide a great deal of information which show cubic Cu_2Se as stable, stiff, ductile and isotropic at room temperature. Existing literature show numerous data on the properties of cubic Cu_2Se, with limited data on the hexagonal Cu_2Se phase [2, 4, 5]. It is in this sense that calculating electronic and elastic properties of hexagonal Cu_2Se will assist in generating this insufficient data. Such data will in turn assist in determining if hexagonal Cu_2Se is a suitable thermoelectric material for solar cells applications. The paper aims to further report on the structural, electronic and elastic features of the hexagonal Cu_2Se at normal temperature.

2 Methodology

A full-potential all-electron density functional theory (DFT) package based on the first principle linearized augmented plane waves calculations was used in this study [9]. An open source Exciting code [9] was used to investigate the structural, electronic and elastic properties of hexagonal Cu_2Se. Generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof revised for solids (PBE_sol) was used for the exchange and correlation functional energy [10]. Throughout the calculation, the k-points sampling of 4 x 4 x 2 was used in the reciprocal space Brillouin zone. A cut-off energy of 500 eV with a force tolerance of less than 0.02 eV/Å for each atom relaxation was considered. The total energy convergence was also based on the convincing sampling mesh of the k-points and the expansion of the eigenfunctions using the chosen size of the basis set. In this way, the calculation time scales linearly with respect to the k-points' weighing and exponentially with respect to the basis set [11]. In addition, the application of ElaStic@exciting was used to determine the second-order elastic constants (SOECs) of hexagonal Cu_2Se, which helps in investigating the elastic properties of the material [12]. From these, the energies and stresses of the distorted structure were calculated. Since the structure is hexagonal, a choice of deformation types of hexagonal material was selected. The deformation types are deformation 0, 1, 3, 4, 8, and 9 [12]. Assumed experimentally observable hexagonal Cu_2Se phase has a space group $P6_3/mmc$ [no. 194] with six (6) atoms per unit cell according to the following Wyckoff atomic positions [13]: Cu^{1+} ions occupy lattice positions 2b (0.000 0.000 0.750) and 2d (0.333 0.667 0.750) in succession, Se^{2-} ions occupying 2c (0.667 0.333 0.750) lattice positions [13].

3 Results and discussion

Structural, electronic and elastic properties of hexagonal Cu_2Se phase were investigated using a full-potential all-electron density functional theory package. Structural properties are characteristics of the material at ground state. The electronic properties help in understanding how materials conduct or resist the flow of electrons. This can be described in terms of the electronic band structure and density of state of the materials. Elastic properties describe the material's deformation behaviour due to external forces.

3.1. Structural properties

Figure 1(a) shows a conventional hexagonal Cu_2Se crystal lattice generated using the xcrysden visualisation program [14], which is used to visualise different crystalline and molecular structures. Geometry optimisation of hexagonal Cu_2Se yielded to the energy versus volume curve presented in Figure 1(b). Based on Figure 1(b), lattice parameters were also calculated to yield $a = b = 8.37$ *bohr (4.43 Å)* and $c = 9.94$ *bohr (5.26 Å)* corresponding with the total energy of -2.22×10^5 *eV* and the equilibrium volume of *594.93 bohr*^{3}. A complete data on calculated equilibrium properties is listed in Table 1. He et al. [15], calculated the lattice parameters of hexagonal Cu_2Se using DFT and found $a = b = 4.12$ *Å* and $c = 6.26$ *Å*. A percentage difference of 7.36% and 17.25% for $a = b$ and c lattice parameters, respectively, was noted. However, no related experimental lattice parameters were obtainable from the literature.

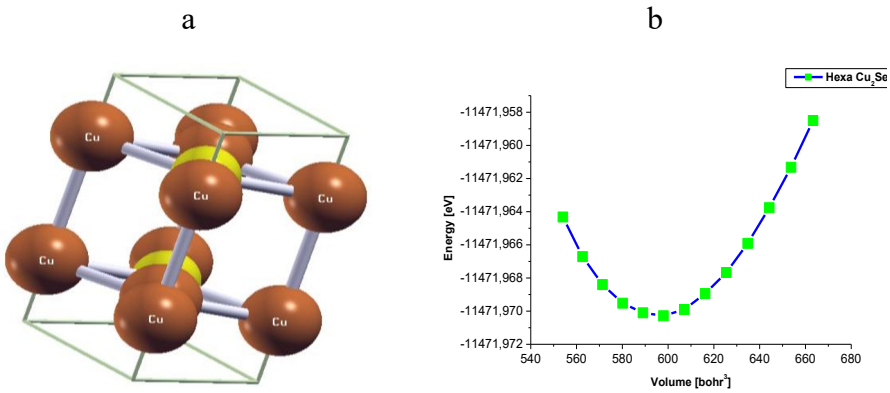

Fig. 1. (a) Lattice structure of hexagonal Cu_2Se, (b) total energy against volume.

Table 1: Unit cell quantities of hexagonal Cu_2Se.

	This work		Theoretical [15]	
Lattice constants (bohr)	$a = b$	c	$a = b$	c
	8.37 (4.43 Å)	9.94 (5.26 Å)	7.79 (4.12 Å)	11.83 (6.26 Å)
Total energy (eV)	-2.22×10^5			
Equilibrium volume (bohr^3)	594.93			

3.2. Electronic properties

Figure 2(a) illustrates the electronic band structure of hexagonal Cu_2Se. The band structure shows, valence bands below the Fermi level and few conduction bands above the Fermi level along high symmetry directions in the Brillouin zone. At the Fermi level, the valence band overlaps the conduction band at Γ and A points which suggests metallic, zero energy band gap behaviour. Lv et al. [16], reported that, if the energy bands have curves which produce a maximum, the effective mass of the charge carriers is negative and associated with p-type conductivity. If the curves produce a minimum, the effective mass of the charge carriers is positive, which suggests an n-type material. In accordance with Figure 2(a), the curvature of the bands is downward, meaning that the charge carriers have negative effective masses: as such, hexagonal Cu_2Se suggests a p-type conductivity. In addition, Figures 2(a) show some flat bands from point Γ up to M, between -4 to -2 eV energy values, which point out that the masses of charge carriers along these directions are substantial, suggesting more occupied deep level states [17]. The total density of states (TDOS) and partial density of states (PDOS) for hexagonal Cu_2Se are presented in Figures 2(b) Like the electronic band structures, the TDOS of hexagonal Cu_2Se system confirm the zero band gap. The system suggests that the nature of the valence band maximum (VBM) is predominantly Cu^{1+} d-like. Such behaviour was also observed in electronic band structures. The TDOS of material demonstrates the existence of a mixture of Cu^{1+} and Se^{2-} ions core electrons s and p-states in region -9 to -7 eV. Furthermore, TDOS also demonstrate a possible fusion of s, p and d-states from the valence band to the conduction band region. Moreover, 4s states manifest in the conduction band region 0 to 6 eV [17]. In consolidation, the electronic band structure and density of states further confirm the metallic character of hexagonal Cu_2Se.

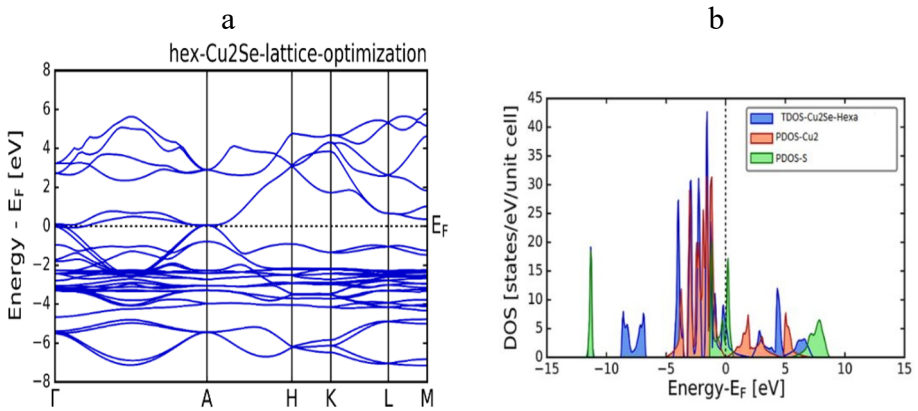

Fig. 2. Calculated (a) electronic band structure of hexagonal Cu_2Se, (b) total density of states (TDOS) and partial density of states (PDOS) of hexagonal Cu_2Se.

3.3. Elastic properties

Elastic properties is the main aspect when describing the stability, ductility, anisotropy and stiffness of materials. Elastic constants were calculated using the ElaStic@exciting [17] interface. Since the system is hexagonal, five independent elastic constants: C_{11}, C_{12}, C_{13}, C_{33}, and C_{44} were considered. Secondary elastic moduli are generated from these primary constants. For hexagonal systems, the following structural stability criteria holds: $C_{11} > 0$, $C_{11} > |C_{12}|, C_{44} > 0, (C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0$ [3, 18]. Table 2 and 3, illustrate the elastic constants and elastic properties of hexagonal Cu_2Se, respectively. All the criteria for structural stability of a hexagonal system as stipulated above are satisfied in this material. The elastic

constants C_{11} and C_{33} signify the resistance to linear compression, whereas C_{12}, C_{13}, and C_{44} denote resistance to shape deformation [19]. In addition, C_{11} and C_{33} describe the stiffness experienced along the crystallographic *a* and *c*-axes, respectively. Shear related C_{12} and C_{13} are responsible for functional stress components along the crystallographic *a*-axis with uniaxial strains along the crystallographic *b* and *c*-axis, respectively. For instance, if the stress in a crystal is applied along the *a*-axis, then the stress components would be able to resolve shear deformation resistance along the *b* and *c*-axis [16]. Lastly, C_{66} also provides additional shear modulus on hexagonal crystals directed along the *a*-axis [15]. According to Al-Qaisi *et al.* [19], $C_{11} > C_{33}$ implies a good compressible material along the *c*-axis than along the *a*-axis. However, if $C_{11} < C_{33}$, it implies that the material is compressible to all lattice compressions. Coming to hexagonal Cu_2Se, $C_{11} < C_{33}$, which signifies that the crystal is more susceptible to all lattice compressions. The elastic constant C_{44} can be used to measure the hardness of a material. A low value of C_{44} in a material, suggest a high shear ability and low hardness [19]. Looking at Table 1, C_{44} = 12.53 GPa, which suggests that the material has a high shear ability. Moreover, C_{44} is the least elastic constant, which signifies that the crystal is susceptible to shear deformations. Considering Table 2, bulk modulus of hexagonal Cu_2Se is greater than the shear modulus, i.e 114.8 > 44.76 GPa, which suggests the parameter limiting mechanical stability is the shear modulus [20]. In the case of the Young's modulus,

Davarpanah et al. [20], explained that Young's modulus measures the stiffness of the materials, and a large value of the Young's modulus means that the material is stiff, as such may not deform easily under applied elastic stress. In addition, the Young's modulus of copper ranges from 110 to 130 GPa, and copper is considered to be malleable and ductile [21]. The calculated Young's modulus of Cu_2Se is 118.83 GPa. This value suggests that hexagonal Cu_2Se is a malleable and ductile material. Bulk and shear moduli values are also used to calculate the Poisson's ratio. The bulk modulus implies resistance to uniform volume compression, the shear modulus reflects how material deform under planar shear deformation so that the Poisson's ratio can predict the ductility or brittleness of the materials [17]. Hexagonal Cu_2Se acquired a Poisson's ratio value of ν = 0.340, which is between 0.000 – 0.500 and is positive. The Poisson's ratio is greater than 0.33, this means that the material is ductile with ionic bonding. Furthermore, this Poisson's ratio also indicate that the material is more tuneable to shear deformation [17]. Karwasara et al. [22] explained that a perfect metallic compound acquires a Poisson's ratio equal or greater than 0.33, this suggests that the system conform to a perfect metallic behaviour. Such findings are also confirmed by the calculated electronic band structures and density of states in sub-section 3.2. Another point to note is that Pugh's indexes and Poisson's ratio of the material are less than 0.5 and greater than 0.26 respectively, demonstrating ductility and ionic bonding, which signifies possible consideration in device fabrication for solar cell applications [17, 22]. Finally, the Zener's anisotropy (A) factor was also calculated. The value was found to be 0.07, which is less than 1.00, and it suggest that the material is anisotropic [22]. Existing literature search could not provide referral information on the elastic properties of hexagonal Cu_2Se phase.

Table 2. Calculated elastic constants of hexagonal Cu_2Se in GPa units.

C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
206.6	103.6	46.75	225.8	12.53	51.47

Table 3: Calculated bulk (B_0), Young's (Y), and shear (G) moduli, Cauchy pressure (C_{12}-C_{44}), in GPa units; Poisson's ratio (ν), Pugh's index (G/B_0), and Zener anisotropy (*A*) of hexagonal Cu_2Se.

B_0	Y	G	C_{12}-C_{44}	ν	G/B_0	*A*
114.8	118.8	44.76	91.08	0.340	0.380	0.070

4 Conclusion

Structural, electronic and elastic properties of hexagonal Cu_2Se were successfully investigated using the first principles calculations. The structural properties which are lattice constants, total energy and volume were successfully calculated. Electronic band structure, total and partial density of states of hexagonal Cu_2Se indicate that, hexagonal Cu_2Se is a metallic material with a calculated band gap of zero. The TDOS further suggest that Cu^{1+} electrons density contribute more than the Se^{2-} electrons density in the hexagonal Cu_2Se deep level conduction. Calculated elastic constants reveal hexagonal Cu_2Se as mechanically stable. Derived Cauchy pressure is positive, which suggests metallic character of ionic bonding. Smallest value of C_{44} in all elastic constants, signifies that the shear deformation can occur easily if shear stresses are applied on the horizontal planes along the vertical direction. Moreover, the bulk modulus, Young's modulus, Pugh's index Poisson's ratio and Zener's anisotropy factor values show ductility, compressibility and anisotropy behaviour of the material and such materials are required in the fabrication of solar cell devices.

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All data used in this paper is with the authors (M Ramoshaba and T Mosuang) and can be made available on request.

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