Structural, electronic, elastic stability and optical properties of rare-earth copper chalcogenides LaCuX$_2$ (X = S and Se), a first principles study

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Abstract. Structural, electronic, and optical properties of rare-earth copper chalcogenides LaCuX$_2$ (X = S, Se) were investigated with density functional theory (DFT). The calculated structural properties agree reasonably well with previous results and experimental data. Calculated elastic constants satisfy the stability conditions for monoclinic structures, which confirms mechanical stability for the compounds. DFT band structure and density of states calculations reveal that the LaCuX$_2$ (X = S, Se) compounds are direct band gap semiconductors. The fundamental gaps were determined at the many-body perturbation theory G$_0$W$_0$ level of approximation, while optical parameters such as dielectric functions, refractive indices, reflectivity and absorption coefficients were examined by solving the TammDancoff-Bethe-Salpeter approximation. The calculated optical energy gaps are between 1.52 and 2.04 eV. From the results obtained, LaCuX$_2$ are stable compounds and posses energy gaps suitable for photo-electrochemical and photovoltaic applications.

1. Introduction

The ternary rare earth metal copper chalcogenides with chemical formula LnCuX$_2$ (Ln = rare-earth metals and X = S, Se), have been studied by various researchers. Investigations include the synthesis and structural characterizations of LnCuX$_2$ (Ln = rare-earth metals, X = S Se) [1, 2, 3]. In others studies the structural diversity and potential applications as promising optical and thermoelectric [4], photo-catalytic [5] and magnetic [6] materials have been reported for the LnCuX$_2$ compounds. Their counterparts, the delafossite rare earth/transition metal copper dioxides, are well studied theoretically and experimentally and have been identified as p-type transparent conducting oxide (TCO) [7, 8] materials.

Synthesis and single crystal determination of the ternary compounds LaCuS$_2$ and LaCuSe$_2$ were reported by Julien-Pouzol [1] and Ijjaal et al. [2] respectively. LaCuS$_2$ crystallizes in a monoclinic P2$_1$/b structure which is built up of sheets of pair arrangements of tetrahedral La$_2$S and CuS$_2$ parallel to the b and c-axis. From x-ray powder diffraction [3] study, LaCuS$_2$ is isostructural to YCuSe$_2$. Similarly, LaCuSe$_2$, which is isostructural to LaCuS$_2$, crystallizes in monoclinic, space group P2$_1$/c structure, with four formula (Z=4) units per cell [2]. The structure consists of layers of CuSe$_4$ tetrahedral units separeted by double layers of LaSe$_7$, and monocapped trigonal prism structures along the a-axis.

Most of the investigations carried out on LaCuS$_2$ and LaCuSe$_2$ are experimental studies of the crystal structure and lattice parameters. Recently Nguyen et al. [5] carried out an experimental study of LaCuS$_2$ combined with mesoporous silica and graphine oxide to investigate photo-catalytic

applications. Also, Li [9] identified $LaCuS_2$ as a potentially good candidate for a transparent p-type conductor considering its gap-modulation when doped with Yttrium (Y). Theoretical studies of physical properties of these materials such as structural, elastic stability, electronic, dynamic and optical properties are lacking in the literature despite their potential technological importance. We are motivated by this to carry out $ab - initio$ calculations to explore the physical, electronic and optical properties of $LaCuS_2$ and $LaCuSe_2$.

In this work, we study the structural, elastic stability and electronic properties of $LaCuX_2$ (X = S, Se) using the density functional theory (DFT) in the Kohn-Sham formulation [10] within the generalized gradient approximation (GGA) PBEsol [11], semi-local modified Becker-Jonhson potential (MBJ) [12] and the hybrid HeydScuseriaErnzerhof (HSE) [13] approximation. Optical properties, including absorption coefficient, absorbance, refractive index, reflectivity and energy loss were studied at the level of G_0W_0-BSE approximation [14, 15].

We consider this work important because simulated electronic structure and optical property studies is a useful tool [16] for identifying potential photovoltaic materials.

2. Method of calculations

All calculations of structural, mechanical, electronic and optical properties of $LaCuX_2$ were carried out within the framework of density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP) [10, 17]. VASP implements a plane-wave basis set and a projected-augmented-wave (PAW) [18] formulation for the description of electron-ion interactions. Groundstate energies were calculated within the Perdew-Burke-Ernzehof generalized gradient approximation as revised for solids and their surfaces, PBEsol [11], for the electron exchange-correlation energy. Equilibrium structure optimization was conducted on the primitive cell structure with energy cut-off of 520 eV and a $4{\times}4{\times}4$ Monkhorst-pack mesh [19] for sampling the Brillouin zone. The k-point mesh sampling was chosen to achieve convergence energies within less than 1 meV/atom. The elastic tensor was calculated for the fully relaxed equilibrium geometry with PBEsol. From the optimized structure DFT band structure calculations were performed PBEsol as well as with the Modified Johnson Becker MBJ [12] potential and hybrid functional Heyd-Scuseria-Ernzerhof (HSE06) [13], to estimate DFT fundamental band gaps. MBJ and HSE normally give better estimates of the fundamental band gap when compared to conventional DFT calculations with local or semi-local exchange-correlation functions. The fundamental gaps were also determined from the so called many-body Green's function approximation G_0W_0 [14, 15]. The optical absorption spectrum was obtained by including excitonic effects using the Tamm-Dancoff, G_0W_0 + BSE [14, 15, 20, 21] approximation. From the optical absorption spectra, the optical band gaps were determined using Tauc plots [22].

3. Results and discussion

3.1. Structural properties

The structural optimization of $LaCuS_2$ and $LaCuSe_2$ units cells by means of total energy minimization for unit cell and atomic position were performed to obtain equilibrium lattice constants. Synthesis and characterizations of structural lattice parameters have been reported and it is known that $LaCuS_2$ and $LaCuSe_2$ both crystallize in a monoclinic crystal, space group $P2_1/b$, with four formula units (Z=4) per cell, [1] and $P2_1/c$ [2] respectively. The numerically optimized crystal unit cells and first Brillouin zone are shown in Figure 1 and 2. From the fully optimized structure of $LaCuS_2$ and $LaCuSe_2$ we derived the ground state properties. The optimized volume, bulk modulus and its pressure derivatives are determined by fitting the total energy to the well-known 3rd order Murnaghan's equation of state (EOS) [23] for this purpose. The energy volume relationship are depicted in Figure 3 and 4. Lattice parameters, angle β for monoclinic crystals, optimized volume, bulk modulus and it's pressure derivative compared to available experimental values are listed in Table 1.

The PBEsol is well-known to describe accurately the behavior of solid [11]. Hence, our calculated structural parameters agree reasonably with experimentally reported [1, 2] values within 2%. Computed cohesive energies have negative values indicating that $LaCuX_2$ are energetically stable compounds.
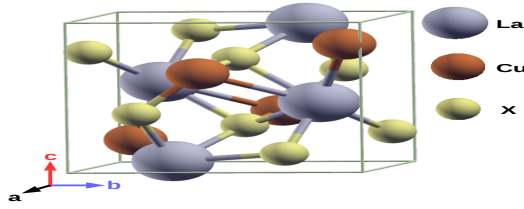
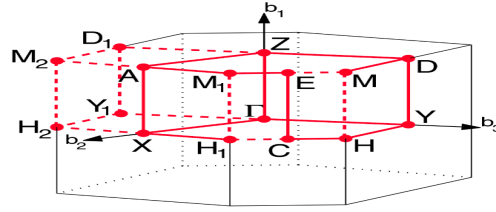**Figure 1.** Craystal structure of LaCuX$_2$.

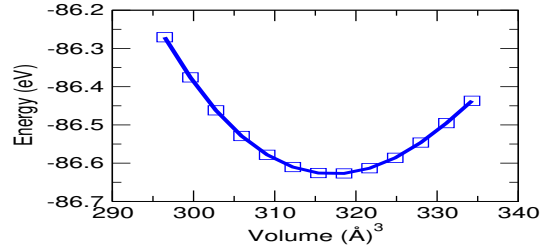**Figure 2.** First Brillious zone of LaCuX$_2$ unit cells.

Figure 3. Variation of total energy as a function of volume of LaCuS$_2$.
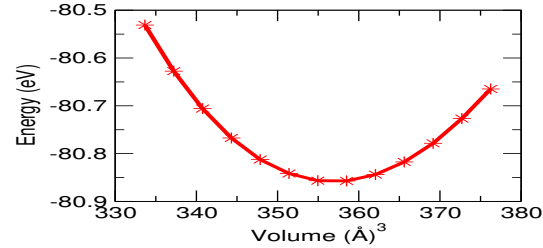

Figure 4. Variation of total energy as a function of volume of LaCuSe$_2$.

Table 1. Computed and experimental lattice parameters a, b, c (Å), volume V_0 (Å^3), angle β, bulk modulus B_0 (GPa), pressure derivatives of bulk modulus B_0' and cohesive energy E_{coh} (eV/atom).

	a	b	c	V	β	B_0	B_0'	E_{coh}
LaCuS$_2$	6.49,6.65[1]	6.82,6.94[1]	7.23,7.33[1]	317.12	82.13,98.73[1]	73.90	5.56	-5.41
LaCuSe$_2$	6.70,6.81[2]	7.51,7.58[2]	7.14,7.20[2]	356.8,369[2]	83.12,97.12[2]	63.44	3.29	-5.05

3.2. Elastic stability

We calculated the elastic constants from the PBEsol optimized structures of LaCuS$_2$ and LaCuSe$_2$ to check their mechanical stability. LaCuX$_2$ are monoclinic crystal structure with 13 independent elastic stiffness constants C$_{ij}$. The calculated values of the elastic constants are listed in Table 2. All monoclinic stability criteria [24] are satisfied and hence the compounds are mechanically stable. There are no available theoretical or experimental C$_{ij}$ values for comparison. Using Hill'S approximation [25] the bulk moduli (B_0) are 79.12, 66.32 (GPa), shear moduli (G) 105.31, 86 (GPa) and Poisson's ratio (ν) both as 0.28 for LaCuS$_2$ and LaCuSe$_2$, respectively. Bulk and shear moduli are measures of a material's response to applied stress. Substituting Sulfur (S) by Selenium (Se) atom bring considerable decrease in bulk moduli and it's pressure derivatives, as well as the shear modulus. This indicates that compressibility increases and resistance to plastic deformations decreases with substitution of Se atom in LaCuX$_2$. The ratio B/G describes the ductility or brittleness behavior of a material. Our calculated values of B_0/G, 1.92 and 1.98 for LaCuS$_2$ and LaCuSe$_2$, respectively, show that the compounds are ductile [26]. Similarly, Poisson's ratio ν values of 0.28 reveal that the compounds are materials with good plasticity, and that the inter-atomic forces are central with an ionic bonding characteristic [27].

3.3. Electronic properties

The fundamental band gaps of LaCuS$_2$ and LaCuSe$_2$ were estimated with PBEsol, MBJ, HSE06 and G$_0$W$_0$ for better estimates and comparisons. The band structure calculated with PBEsol along high symmetry directions, with total (TDOS) and partial densities of states (PDOS), are shown in

Table 2. The computed thirteen independent elastic constant of LaCuX$_2$.

	C_{11}	C_{12}	C_{13}	C_{15}	C_{22}	C_{23}	C_{25}	C_{33}	C_{35}	C_{44}	C_{46}	C_{55}	C_{66}
LaCuS$_2$	159.82	60.9	56.80	4.04	104.7	49.52	-3.25	127.55	-4.47	55.41	6.68	35.46	46.51
LaCuSe$_2$	132.89	48.09	48.25	2.26	80.58	46.43	-0.07	113.3	-2.39	42.83	4.20	29.56	39.96

Table 3. Calculated and experimental band gap (eV) of LaCuX$_2$ compounds.

	PBEsol	MBJ	HSE06	G_0W_0	BSE			Exp.
					a	b	c	
LaCuS$_2$	1.24	1.56	2.31	2.39	2.04	1.97	1.98	2.23[9]
LaCuSe$_2$	0.85	1.41	1.87	1.85	1.64	1.52	1.52	

Figure 5 and Figure 6. The calculated band structures reveal that LaCuX$_2$ are direct band gaps semiconductors with gaps at the Γ point. The upper valence band (VBM), or Fermi-level is adjusted to zero. For the LaCuX$_2$ materials the VBM is dominated by hybridization of Cu(d) and Se(s) with a small contribution from La(d), while the lower conduction band (CBM) is dominated by La(d). The computed and available experimental band gaps are listed in Table 3. Our computed minimum fundamental band gaps for LaCuS$_2$ from PBEsol, MBJ, HSE06 and G_0W_0 are 1.24, 1.56, 2.31 and 2.39 eV, respectively. As expected, the GGA-PBEsol value under-estimates the experimental optical gap of 2.23 eV, while G_0W_0 gives a value which is larger than the measured optical gap. MBJ and HSE06 give values closer to the experimental value than PBEsol, as is commonly expected [28]. For the G_0W_0-BSE estimates (see discussion in next section), polarization of incident radiation is taken into account and optical anisotropy is evident. The best estimate we have for the optical gap, 1.97-2.04 eV, compares well with the experimental value. The results suggest that our calculated G_0W_0-BSE estimate of the optical band gap for LaCuSe$_2$ will be a good indicator of the value of this compound. We believe that one of the goals of material design is to tailor the band gap for desired applications. The substitutions of sulfur (S) by selenium (Se) atom in LaCuX$_2$ narrows the band gap to an energy around the recommended Shockley-Quiesse [29] equation band gap limit for ideal solar cell devices. These results are encouraging and suggest further study of the LaCuSe$_2$ compounds.
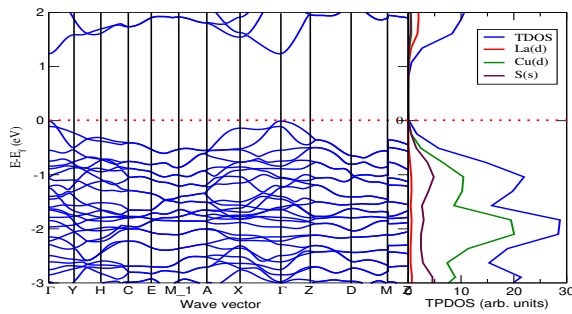
Figure 5. Electronic band structure, TDOS and PDOS of LaCuS$_2$.
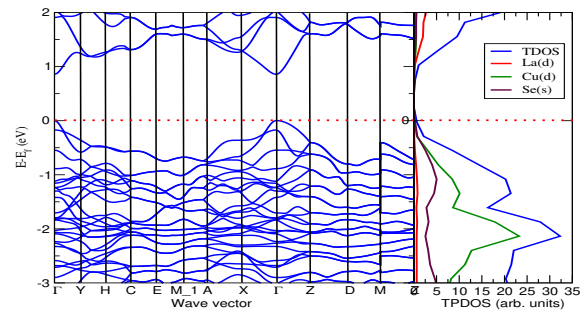
Figure 6. Electronic band structure, TDOS and PDOS of LaCuSe$_2$.

3.4. Optical properties

We investigated the optical properties of LaCuS$_2$ and LaCuSe$_2$ from the complex dielectric function $\epsilon(\omega)=\epsilon_1(\omega)+i\epsilon_2(\omega)$. The absorptive part, which is the imaginary dielectric function $\epsilon_2(\omega)$ can be calculated from momentum matrix elements between the occupied and unoccupied wave function [30]. The dispersive part, the real dielectric function $\epsilon_1(\omega)$, can be evaluated from the imaginary

Table 4. Computed static dielectric $\epsilon_1(0)$x, $\epsilon_1(0)$y, $\epsilon_1(0)$x, refractive index $n(0)$x, $n(0)$y, $n(0)$z and reflectivity $R(0)$x, $R(0)$y, $R(0)$z of LaCuS$_2$ and LaCuSe$_2$ compounds.

Compounds	$\epsilon_1(\omega)$			Refractive index			Reflectivity		
	$\epsilon_1(0)$x	$\epsilon_1(0)$y	$\epsilon_1(0)$z	$n(0)$x	$n(0)$y	$n(0)$z	$R(0)$x	$R(0)$y	$R(0)$z
LaCuS$_2$	4.11	3.45	4.48	2.03	1.85	2.11	0.33	0.20	0.23
LaCuSe$_2$	5.61	4.47	6.45	2.38	2.12	2.55	0.33	0.20	0.23

part the $\epsilon_2(\omega)$ using the Kramers-Kronig relations. Here we report the absorption coefficient $(\alpha(\omega))$ from which we estimated the directional x, y and z spectral absorption using the Tauc approach applied to the G_0W_0+BSE results. The band gap values are listed in Table 3, while the Tauc plots are shown in Figures 9 and 10. For the study of LaCuX$_2$ compounds the imaginary dielectric function $\epsilon_2(\omega)$ which is a frequency dependent is calculated using the G_0W_0+BSE approach in the energy range 0 - 8 eV depicted in Figure 7 and 8. This approach provides a reliable two particle interaction and electronic excitonic description [32]. The $\epsilon_2(\omega)$ optical spectra are obtained from the inter-band transition which are found to be consistent with our computed band structure. Optical spectra absorption peaks arises because of inter-band transition from top valence band (VB) to the bottom of the conduction band (CB). In Figure 7 and 8 the onset peaks of strong absorption occur at about 2.0 eV and 1.60 eV for LaCuS$_2$ and LaCuSe$_2$ respectively, which are consistent with our calculated band gaps from HSE06, G_0W_0, BSE and experiment. The static refractive index and reflectivity, which can also be derived from the imaginary and real parts of the dielectric functions using equations from reference [31], are listed in Table 4.
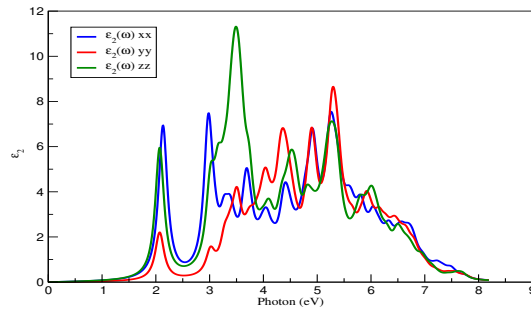

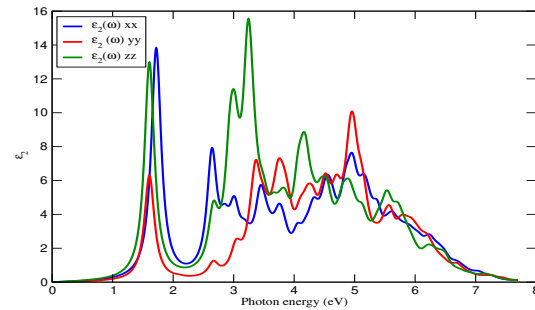**Figure 7.** Imaginary dielectric $\epsilon_2(\omega)$ of LaCuS$_2$.

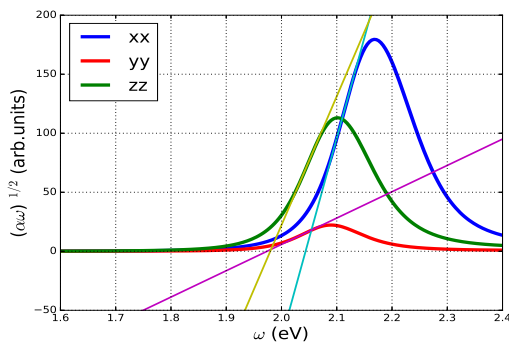**Figure 8.** Imaginary dielectric $\epsilon_2(\omega)$ of LaCuSe$_2$.

Figure 9. Tauc plot of absorption spectra of LaCuS$_2$.
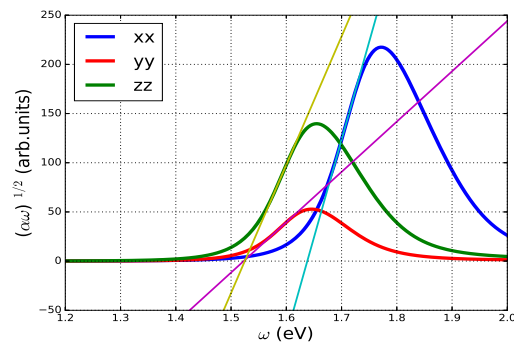

Figure 10. Tauc plot of absorption spectra of LaCuSe$_2$.

4. Conclusions

We use DFT and post-DFT techniques successfully study structural, electronic, elastic stability and optical properties of $LaCuS_2$ and $LaCuSe_2$ to fill the gap in the literature. Electronic band structures calculated from the DFT-PBEsol approximation show that $LaCuS_2$ and $LaCuSe_2$ are Γ point direct band gap semi-conductors. Calculated elastic constants verify the mechanical stability of $LaCuS_2$ and $LaCuSe_2$. Study of optical properties from many-body perturbation theory reveals that $LaCuSe_2$ has potential to absorption in the visible range. The computed energy gap from BSE calculations are 2.04 and 1.64 eV of $LaCuS_2$ and $LaCuSe_2$ respectively. This is favorable for photo-electrochemical and photovoltaic applications. $LaCuSe_2$ has potential for absorbing in the visible region, while $LaCuS_2$ has potential as a complementary absorber in a multi-junction solar cell.

5. Aknowledgements

6. References

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