Electronic, optical and elastic properties of AgCuS

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DFT calculation is used to investigate the structural, electronic, optical, and elastic
properties of AgCuSe and AgCuS. The calculations are performed using the ATK with
generalized gradient approximation (GGA) in combination with Hubbard U correction
parameters for both structures. The calculated band gap energies and partial density of
state reveal that AgCuS has semiconductor properties unlike this AgCuSe has a metallic
nature. The optical properties, real and imaginary parts of dielectric function are obtained
for the energy range of 0 to 5 eV. Elastic stiffness coefficients (*Cij*), bulk modulus (*B*),
shear modulus (*G*), and Young modulus (*E*) have been calculated.

1. Introduction

Chalcogenide semiconductors containing silver and copper are considered interesting
research objects. With cation-cation and anion-anion substitution, changes in the crystal structure
occur [1-5]. It is known that changes in structure affect the physical properties of crystals, which
leads to the importance of studying the structure and electronic properties of semiconductors.
During theoretical calculations, it is possible to predict the electronic and structural characteristics
of the crystal, as well as their phase transitions. Therefore, the electronic properties of
chalcogenide semiconductors are studied theoretically [6-10].

The main reason for studying the AgCuS and AgCuSe structures is due to their interesting
and complex crystal structure. As is known from experimental work, the compound has two
phases: a low-temperature β-phase and a high-temperature α-phase [11,12]. The authors of
experimental work [13] report that at low temperatures the structure has two tetragonal and
orthorhombic structures. In theoretical work [14], the stabilities of the three structures and their
electronic structures were investigated using the Vienna Ab initio modeling package (VASP) with
DFT calculations. It has been established that the physical properties of a crystal differ depending
on the position of the atoms of the crystal and the direction of the chain. In theoretical work [15],
the high-temperature phase of the compound and the structure under pressure were studied [16].
Many studies have shown that the structure has a p-type conductivity with a significant
thermopower at room temperature [17]. For two structures of AgCuS and Ag_3CuS_2 theoretical and
experimental investigations were carried out to study the electronic structure for photovoltaic
applications. Calculations showed that AgCuS has a direct band gap with a gap width of 1.27 eV
[18].

From a review of all theoretical studies, it is clear that in the literature only one work in which the band gap is overestimate the experimental data. Taking into account that the accuracy of the optical parameters depends on the band gap, at the first step we calculate band gap in accordance to experimental results. In the second step, optical parameters were calculated and presented. Also, knowledge about elastic parameters of compounds plays a very important role in their application, taking into account that they are absent in the literature, in this work elastic parameters were calculated and presented.

2. Computational details

DFT calculations have been performed for the electronic optical properties' investigation of AgCuS compound using Atomistic Toolkit-Virtual Nanolab (ATK-VNL) [19]. In the present study exchange-correlation interaction of electrons is described by generalized gradient approximation (GGA) based on a local combination of atomic orbitals (LCAO) method. Valence electrons of elements choosen as: Ag-[Kr] $4d^{10}$ $5s^1$, Cu-[Ar] $3d^{10}$ $4s^1$, S-[Ne] $3s^2$ $3p^4$, Se-[Ar] $3d^{10}$ $4s^2$ $4p^4$. As we know GGA and LDA underestimate band gap values so in this calculation we will use Hubbard-U correction. The Brillouin zone integration has been performed using $5\times5\times5$ Monkhorst-Pack grid [20], respectively. The mesh cut-off of 150 Ry has been used for AgCuS(Se) for all configurations. All structures before analyses were optimized with the force and stress tolerance 0.01 eV/Å, 0.01 GPa respectively.

3. Result and discussion

AgCuSe and AgCuS compounds crystallize in different space groups namely orthorhombically, in space group Pmc21 (26), and terogonally P4/nmm (129) with 12 and 8 atoms per unit cell respectively. The primitive cell of AgCuS and AgCuSe were shown in Fig. 1. After optimization of structures obtained for the lattice parameter value are given in Table 1. These results were in good agreement with previous theoretical and relatively consistent with the experimental results [11,14]. It must be noted that using GGA - SG15 using Hubbard U correction give the best result in other theoretical works [21-25].

Table 1. Structure parameters and bond length of AgCuS and AgCuSe.

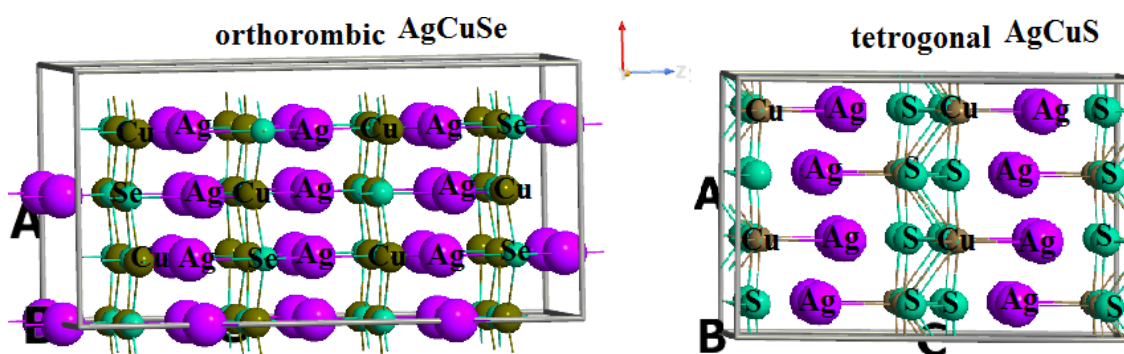|	Lattice parameters (Å)				Bond-length (Ag-S(Se))	Bond-length (Ag-Cu)	Bond-length (Cu-S(Se))
	a	*b*	*c*	volume			
AgCuS	4.05	6.61	7.96	106.99	2.48	3.38	2.31
AgCuSe	4.08	4.08	6.31	105.93	2.87	2.54	2.41

Fig. 1. Crystallographic structure of AgCuSe and AgCuS in orthorhombic and tetragonal symmetry.

After optimization of AgCuS and AgCuSe compounds the electronic band structures have been investigated and presented in the energy range of −3 eV to 3 eV in Fig. 2. As can be seen from the figure calculated band gap of compounds AgCuS and AgCuSe using Hubbard-U (for Cu atoms U=4eV) correction is found to be 1.18 eV and 0eV respectively. This result is in good agreement with other available experimental [18, 26] and theoretical [14,17] results. Compared to an experimental investigation done by Guin et al [17], for AgCuS compound they found a band gap of 0.9eV. But unlike this investigation, carried out for AgCuS using HSE06 method overestimated this result and the band gap was equal to 1.27eV [18]. Taking into account that the in our calculation band gap value is more consistent with experimental data 0.9eV [17], so we did not use the pseudojo pseudopotential to increase the band gap and carried out further optical and elastic properties investigations using GGA - SG15 with Hubbard U parameter. The direct gap is localized at the Γ point. The second nearest VB maximum at the Z point, 0.18eV below the top of the VB. Fermi surfaces is illustrated in Fig. 3.
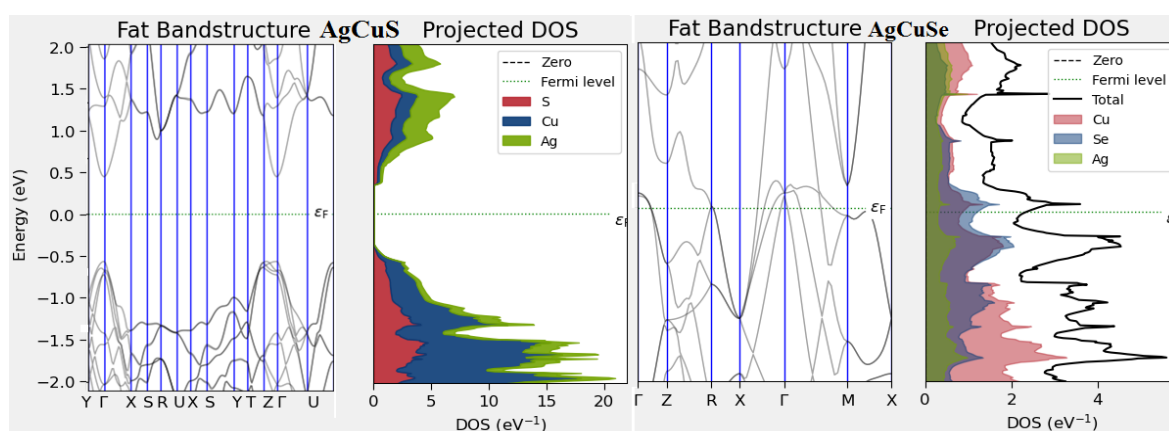

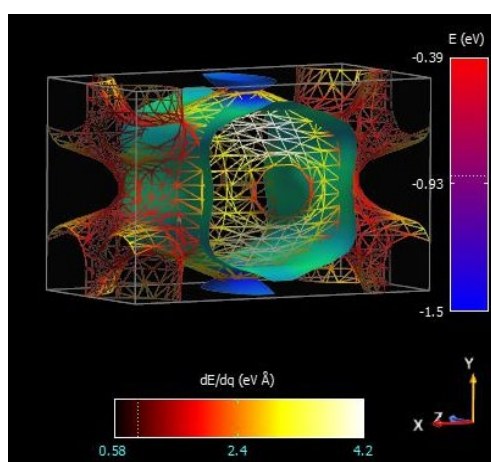*Fig. 2. Band structure and DOS for AgCuS (left) and AgCuSe (right).*

Fig. 3. Fermi surfaces for AgCuS compound.

From the calculated band structure for AgCuSe compound, it is obvious that valence and conduction band near the Fermi level overlap with each other which indicate the semimetallic properties of the compound. This result is in good agreement with other theoretical data [14]. Also, experimental result [26] show that AgCuSe has semimetallic properties. Using density of states (DOS) we analyze the energy distribution of different electronic states. We plot the partial density

of state (PDOS) for AgCuS and AgCuSe together with electronic structure in the left and right panels in Fig. 2 respectively.

The degree of spatial localization of the electron is determined by the electron localization function (ELF). This method displays the probabilities of an electron pair in multi-electron systems, and the bond between atoms can be determined from the ELF graph. In our case (Fig.4), one can see a slight localization of the charge near the Se atom near the silver atoms. This localization means a small amount of covalent bonding between the S and Ag atoms.
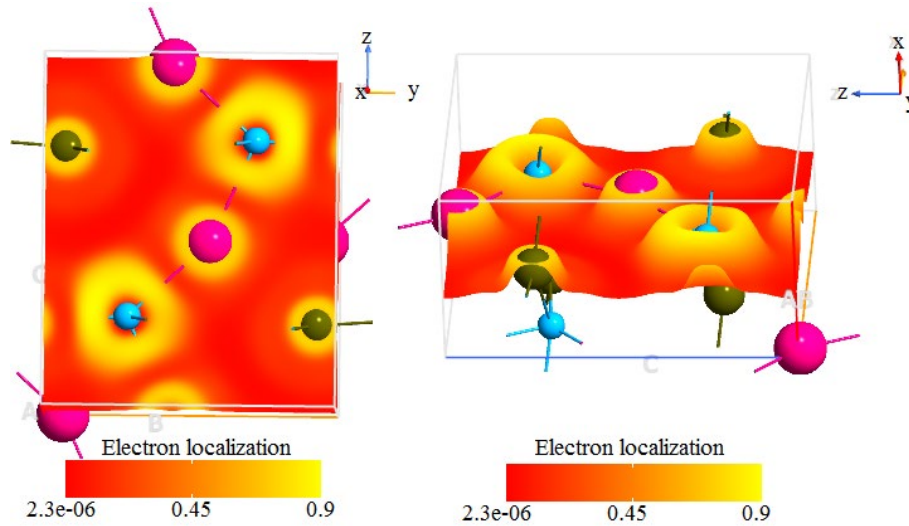

Fig. 4 Electron localization function isosurfaces of AgCuS.

From the PDOS result, it obvious that the VB maximum of AgCuS is mainly from the hybridization of Cu-d and S-p (-0.82-(-1.3) eV). The lower conduction band in the range of 0.73 eV to 2 eV mainly contributed S- p state. So, the Fermi level is mainly from Cu-d, S-p and Ag-d states. For AgCuSe compound PDOS analysis in contrast to AgCuS shows metallic nature so, VB and CB overlap with each other in the vicinity of the fermi level.

As we know tetragonal crystals has six independent elastic constants, C11, C33, C44, C66, C12, C13. These results together with calculated bulk modulus, shear modulus, Young's modulus are presented in Table 2. If we compare the elastic moduli obtained in this work with the elastic moduli of known solid materials, we can see that the low value of Bulk moduli indicates that this structure cannot resist volume deformation and is very easy to compress. Such behavior is also affirmed by the shear modulus value. It must be noted that there are not any experimental or theoretical results for comparing our results for elastic constants.

Table 2. Calculated elastic parameters for AgCuS compound at ambient conditions.

Module	C11	C33	C44	C66	C12	C13	
	119.09	36.33	14.96	22.41	38.45	45.12	

	Reuss	Voigt	Hill
Bulk module	34.16	51.93	43.09
Shear module	15.15	19.93	1.54
	X	Y	Z
Youngs module	62.90	65.75	16.71

The real part (ε_1) and imaginary part (ε_2) of complex dielectric function (ε) and absorption (*a*) were calculated using the dielectric tensor. From Fig. 5, it can be noted that dielectric function in xx, yy and zz directions are almost similar in pattern indicating isotropic structure.
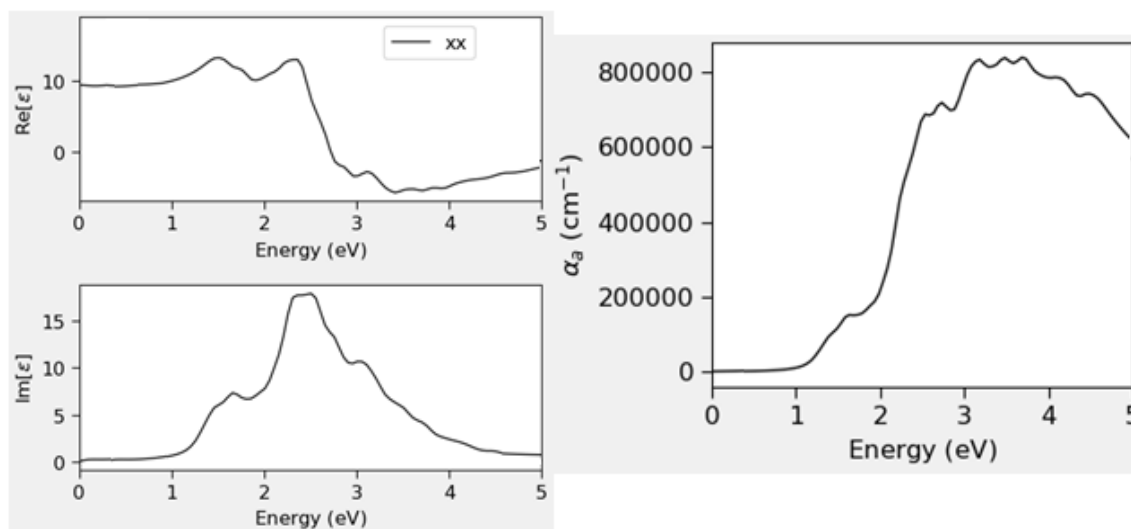

Fig. 5. The real (top), imaginary (bottom) parts of dielectric function and absorption coefficient.

Calculated spectra of e2 (w) and e1 for AgCuS are shown in figure 4. As we can see from Fig. 4 the peak located in the region of 1.54-1.83eV is first peak in imaginary spectra. This peak is associated with transitions of electrons from VBM to CBM which is mainly originated from Cu-d, S-p and Ag-d states according to PDOS. The main peak in absorption is located at 2.3eV. Illustrated absorption is in good agreement with experimental results [27, 28].

4. Conclusions

The structural, electronic, and optical performance of AgCuS and AgCuSe compounds were investigated based on first-principle calculations. In this study, structural properties showed the semiconductor and metal nature AgCuS and AgCuSe materials respectively.

AgCuS is a direct band semiconductor with the transition along $\Gamma \times \Gamma$ symmetry. The calculated band gap value using Hubbard U correction is ~1.18 eV in fairly good agreement with the previous experimental results. The imaginary and real parts of dielectric functions are highly isotropic along x, y, and z-axis. In mechanical calculations, smaller values of shear modulus and bulk modulus indicate that this structure cannot resist volume deformation and is very easy to compress. Bulk moduli indicates that this structure cannot resist volume deformation and is very easy to compress. Such behavior is also affirmed by the shear modulus value.

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