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The study of structural, elastic, electronic and optical properties of $ScAgSe_2$: A First principles study

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ABSTRACT
The structural, elastic, electronic and optical properties of a cheap scandium silver di-selenide are studied using first-principles density functional theory (DFT). The optimized structural parameters are found to be in good agreement with the experimental results. The mechanical stability of $ScAgSe_2$ compound has been theoretically confirmed using the Born criteria. This material shows ductile behavior in nature. The electronic band structures and electronic density of states are calculated. The electronic band structures show semiconducting characteristics of this compound. The calculated energy gap is 0.674eV for PBE potentials. Moreover, optical functions are calculated and discussed for the first time. The reflectivity is found to be high in the IR-UV regions up to ~16.55 eV for $ScAgSe_2$ thus showing promise as good coating materials.
KEYWORDS: $ScAgSe_2$, trigonal crystal, elastic properties, electronic properties, optical properties

I. INTRODUCTION

In the past decade the number of papers published on the I-III-VI_2 compound semiconductors has increased remarkably [1]. A considerable amount of effort has been invested to gain a better and deeper understanding of the electronic, electrical and optical properties of these compounds, since some of these materials have potential for practical applications in the fabrication of devices [2, 3], for instance, in non-linear optics, light emitting diodes, photovoltaic optical detectors and solar cells. $CuInSe_2$, whose binary analogue is $Cd_{0.5}Zn_{0.5}Se$, is one member of this family of compounds which was originally studied by Hahn et al. [4]. It crystallizes in the chalcopyrite structure with lattice parameters a ~ 5.785 Å and c/a = 2 at room temperature [5]. The melting point of this compound has recently been reported [6] to be 987 °C. Two solid state phase transformations at 810 °C [7] and 665 °C [6] have been observed by differential thermal analysis (DTA). Indications of similar transitions can also be detected [8] from the discontinuities in the temperature dependence of the thermoelectric power data.

The optical properties of $CuInSe_2$ have been studied by [9]. They show the semiconducting nature of the compound with the energy gap of 1 eV. At energies well above the edge there exists an additional optical absorption due to forbidden direct transitions with the same characteristic gap energy. The additional absorption may be caused either by the polarization dependence of the selection rules between valence and conduction band states or by the admixture of copper d states to the uppermost valence bands. $CuInSe_2$ has a direct band gap between 0.94 and 1.06 eV [10, 11], and depending upon the growth and annealing conditions, in contrast to its II-VI binary analogues, it can be made either n- or p-type [12, 13]. The n-type conductivity has been reported [14- 18] for samples prepared by in-diffusion of Cu and In and heat-treatment under minimum selenium pressure.

On the other hand, environmental and energy resource concerns have increased, greater stress has been placed on development of renewable energy resources such as photovoltaic electric generators. $CuInSe_2$/CdS, heterojunction solar cells are currently one of the most promising technologies because it is likely that only polycrystalline or amorphous thin-film solar cells could be fabricated in sufficiently large volumes and at sufficiently low costs to be competitive with conventional bulk power sources as well as for the currently tested polycrystalline or amorphous materials only $CuInSe_2$: based heterojunction solar cells have been demonstrated to achieve greater than 14% efficiency [19]. Because of the negative

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impact of global warming after burning the fossil-fuels, the exploration of alternating energy sources e.g. thermoelectric energy generation has become great interest in the past decades. Semiconducting materials are enabling to convert heat into electricity. These materials are also used in solid state cooling. The efficiency of thermoelectric materials is determined by the dimensionless thermoelectric figure of merit ZT, shown as

$$ZT = \frac{S^2\sigma}{\kappa}T = \frac{S^2\sigma}{\kappa_e + \kappa_l}T \quad (1)$$

Where, S is the Seebeck coefficient, σ the electrical conductivity, κ_e, and κ_l are electronic and lattice components of the total thermal conductivity (κ) and T the absolute temperature. The numerator $S^2\sigma$ is called the power factor. It is essential to enhance the power factor in addition to decrease the thermal conductivity for potential thermoelectric materials. The materials having ZT value about unity or greater than unity are excellent candidates for thermoelectric properties. The optical properties of $CuInSe_2$ have been intensely investigated. The experimental data that reported are for the energy range near the fundamental absorption edge. However, the results published by various authors are contradictory, and even the fundamental gap energies scatter widely. This effect gives rise to high intrinsic defect concentrations which influence not only the electrical but also the optical properties of $CuInSe_2$ [20]. The experimental results for the electronic band structure of $CuInSe_2$ which have been derived by them from optical absorption, electro reflectance, reflectivity, electron energy loss and photoemission spectra are critically reviewed. The band structure parameters for the energy range near the fundamental edge have discussed in detail. They have shown that the experimental results can be at least partly understood in terms of the calculated band structure of $CuInSe_2$.

In this research, we have presented first-principles study of electronic, optical, thermodynamic and thermoelectric transport properties of $ScAgSe_2$ by using density functional theory (DFT). The calculated band structure of $ScAgSe_2$ confirms the semiconducting nature and the possibility of high thermoelectric performance.

II. METHOD OF CALCULATIONS

All calculations of $ScAgSe_2$ have been carried out by Cambridge Serial Total Energy Package (CASTEP) code in the framework of density functional theory (DFT) using generalized gradient approximation (GGA) [21]. The electronic exchange correlation energy has been taken into account under the generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof (PBE) [22].

The ultrasoft Vanderbilt-type pseudopotentials for Sc, Ag, Se atoms have been employed to represent the interactions between ion and electron [23]. The calculations used a planewave cutoff energy 350 eV for all cases. For the sampling of the Brillouin zone, 7×7×4 k-point grids generated according to the Monkhorst-Pack scheme [24] are utilized. These parameters are found to be sufficient to lead to convergence of total energy giving geometrical configuration. Geometry optimization was achieved using convergence thresholds of 5×10^{-6} eV/atom for the total energy, 0.01 eV/Å for the maximum force, 0.02 GPa for the maximum stress and 5×10^{-4} Å for maximum displacement. The reciprocal space integrations are performed by using the tetrahedron method with a k-mesh of 120 k-points in the irreducible wedge of Brillouin zone (BZ).

II (A). STRUCTURAL PROPERTIES

The equilibrium crystal structure of $ScAgSe_2$ is shown in Fig. 1. The $ScAgSe_2$ is a trigonal crystal with space group P-3m1 (#164). The optimized lattice parameter is a=3.894 Å, c= 6.589 Å which is very close to the experimental (3.8779 Å, c = 6.6501 Å) [25].

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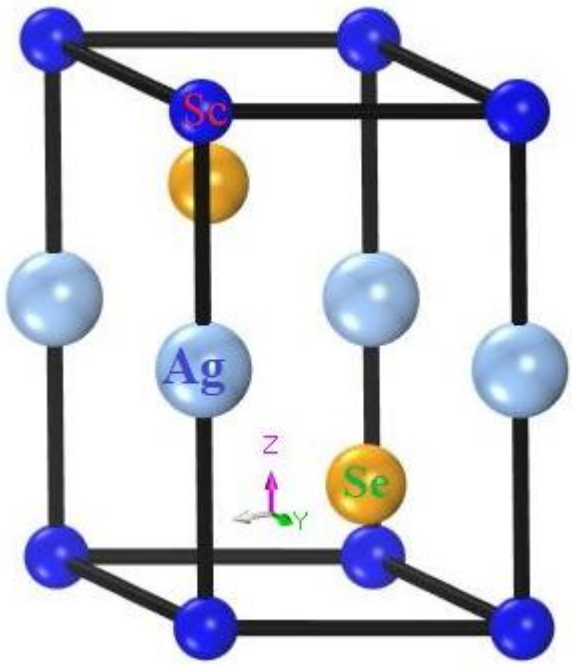

Fig. 1 Equilibrium crystal structure of $ScAgSe_2$.

Table 1. Atomic coordinates of $ScAgSe_2$.

Atom	x/a	y/a	z/a
Sc	0	0	0
Ag	0	0	0.5
Se	0.333	0.667	0.235

II (B). ELASTIC PROPERTIES

The elastic constants are crucial parameters that determine the responses of the compounds to applied stress or strain. Hence we are interested to calculate elastic constants of trigonal $ScAgSe_2$ compound at ambient condition for the first time. A compound is considered to be mechanically stable if the single crystal elastic constants Cij satisfy the well-known Born criteria [26]. In the case of trigonal crystals, the stability conditions are

$$C_{11} - |C_{12}| \rangle 0 \quad (2)$$

$$(C_{11} + C_{12})C_{33} - 2C_{13}^2 \rangle 0 \quad (3)$$

$$(C_{11} - C_{12})C_{44} - 2C_{14}^2 \rangle 0 \quad (4)$$

The compounds under consideration satisfy these criteria quite well and are therefore, mechanically stable. One of the most widely used malleability indicators of materials is paugh's ductility index (G/B) [27]. If the G/B< 0.5 the material will show ductile behaviour, while G/B > 0.5 the material is brittle. According to paugh's ductility index (G/B) the $ScAgSe_2$ compound show ductile behaviour. The knowledge of elastic anisotropy is important in many applications such as phase transformations, dislocation dynamics, development of microcracks, and other geophysical applications. The elastic anisotropy, $A = 2C_{44}/ (C_{11}–C_{12})$ is quantified by Zener [29]. The calculated value of anisotropy is 0.6.

Table 2 Values of calculated and experimental lattice constants a (Å), elastic constants Cij (GPa), Bulk moduli B (GPa), Shear moduli G (GPa), Young's moduli E (GPa), B/G values, anisotropy factor A, for $ScAgSe_2$.

a=c	b	C_{11}	C_{12}	C_{13}	C_{14}	C_{33}	C_{44}	B	G	E	A
3.894	6.589	105.097	43.095	45.568	-10.317	109.12	27.484	65.28	27.96	42.69	0.6

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III (C). ELECTRONIC PROPERTIES

The electronic properties play an important role in measuring the technical scope of the materials. Therefore, we calculate the band structures and density of states of $ScAgSe_2$.

The electronic band structure of $ScAgSe_2$ is shown in Fig. 2. No overlapping between the valence band and conduction band occurs at the Fermi level. Moreover, the conduction band minimum is located at L point and valence band maximum are located at A point. Thus indicates indirect band gap semiconducting behavior of $ScAgSe_2$ compound. The calculated band gap is 0.674eV for PBE potentials. Our calculated band structure confirms that $ScAgSe_2$ is indirect band gap semiconductor with flat valence and conduction band. However, the flat band semiconductors are expected for good thermoelectric materials.

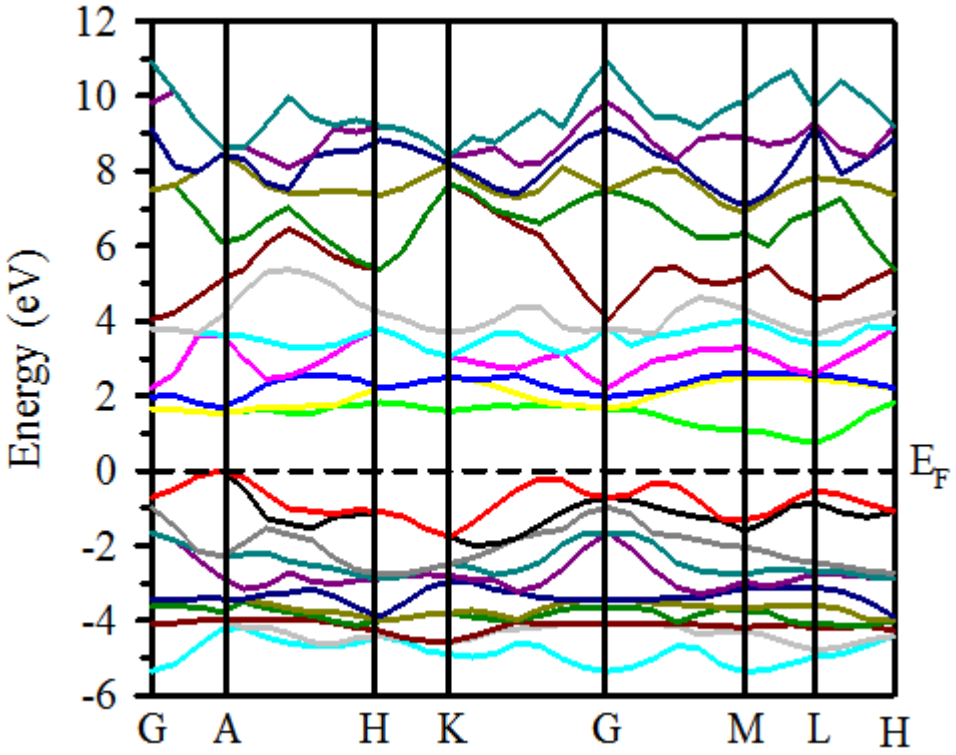

Fig.2 The band structure of $ScAgSe_2$.

To get insight of $ScAgSe_2$ structure, the DOS results of the materials were computed within PBE potential, as sketched in Fig. 3. The DOS at the Fermi level is zero, which proves the semiconducting nature of the materials and confirms the band structure results.

The valence band in the lower energy partition from −5 to -2 eV is dominated by the Sc-3d and Ag-4d and the energy partition from -2 to 0 eV is dominated by the hybridization between Sc-3d, Ag-4d and Se-3d. While in the conduction band the energy states launched mainly by from 0.036 to 5 eV are the hybridization between Sc-3d and Se-3d. The energy states from 5 to 8.3 eV are the hybridization between Sc-4s, Se-4s and Se-4p. the energy states from 8.3 to 11 eV are contributed by the hybridization between Sc-4s, Se-4s and Se-4p.

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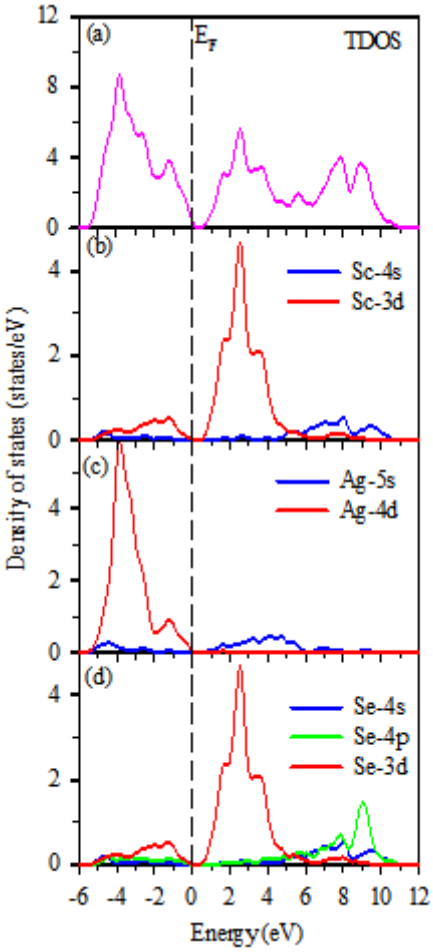

Fig. 3 The Density of states for $ScAgSe_2$.

II (D). OPTICAL PROPERTIES

The analysis of the optical properties of solids helps to give a better understanding of the electronic structure. All calculations are performed for the energy range up to 20 eV of $ScAgSe_2$.The study of optical properties is essential because it helps to understand the electronic properties. Different optical properties serve different purposes, e.g. the refractive index and absorption coefficient is necessary to designing the semiconductor optoelectronic devices. The dielectric function, $\epsilon(\omega)$ is a crucial parameter to describe the optical properties of any homogeneous medium. The function is expressed as $\varepsilon = \epsilon_1(\omega) + i\epsilon_2(\omega)$. The imaginary part $\epsilon_2(\omega)$ is obtained from the momentum matrix elements between the occupied and the unoccupied electronic states and calculated directly by using the following Eq.3 [32].

$$\varepsilon_2(\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{k,v,c}\left|\psi_k^c\left|\vec{u}.\vec{r}\right|\psi_k^v\right|^2\delta(E_k^c - E_k^v - E) \quad (5)$$

Where $\vec{u}$ is used as the unit vector to describe the polarization of the incident electric field, ω is the frequency of light, e is electronic charge, $|\psi_k^c|$ and $|\psi_k^v|$ are the conduction and valence band wave functions at k, respectively. Other optical constants, such as refractive index, loss function, absorption spectrum, reflectivity, and conductivity can be calculated by using Eq. 49 to 54 in ref. [33].

It is observed that the real part ε_1 goes through zero from below at about 17.5 eV and the imaginary part ε_2 approaches zero from above at about 15.93 eV for $ScAgSe_2$.

The peak of the imaginary part of the dielectric function is related to the electron excitation. It is

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clear from the figure that $\varepsilon_2(\omega)$ shows single peak at ~2.1395 eV.

The refractive index and extinction coefficient are illustrated in Fig. 4 (c) and (d), respectively. The calculated static refractive index n (0) is found to be 3.75. The absorption coefficient spectra are displayed in Fig. 7 (e). It is evident from band structures (Fig. 2) that the materials have 0.674 eV energy gap and hence the photoconductivity starts at photon energy (0.674 eV) for each of the phases that is shown in Fig. 7 (f). The maximum optical conductivity was observed at photon energy of ~9.05 eV.

The reflectivity spectra R(ω) and electron energy loss spectra L(ω) are shown in Fig. 7 (g) and Fig. 7 (h), respectively. The reflectivity values of the studied perovskites are high between 0 and ~16.55 eV photon energy, reaching maximum of ~84%. It implies that $ScAgSe_2$ can be used as good coating materials in the IR-UV region up to ~16.55 eV.

The loss function, L(ω), unfolds the energy loss of a fast electron passing through a material. It is observed that L(ω) exhibits sharp peaks at 16.55 eV. This peak represents the feature that is associated with plasma resonance, and the corresponding frequency is called bulk plasma frequency.

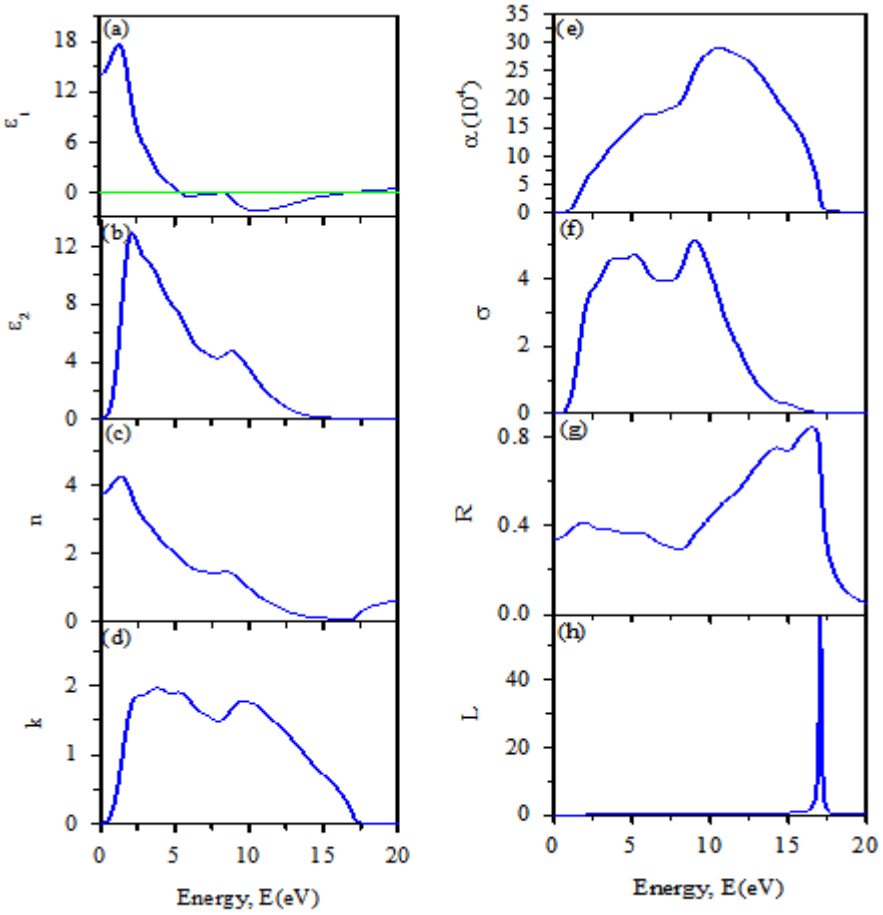

Fig.4 The (a) real part of dielectric function, ε_1; (b) imaginary part of dielectric function, ε_2; (c) refractive index, n; (d) extinction coefficient, k; (e) absorption, α; (f) real part of conductivity, σ; (g) loss function, L and (h) reflectivity, R for $ScAgSe_2$ of polarization vector [100] corresponding to the energy.

Further this peaks correspond to irregular edges in the reflectivity spectrum (Fig. 7 (g)), and hence an abrupt reduction occurs at these peaks values in the reflectivity spectrum and it correlates with the zero crossing of ε1(0) with small ε2(0), shown in Fig. 7 (a, b).

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CONCLUSIONS

We have studied the structural, electronic and optical properties of $ScAgSe_2$ using the density functional theory within GGA. The calculated lattice parameter is in good agreement with the available experimental and theoretical data. The calculated energy bands indicate that $ScAgSe_2$ is an indirect band gap semiconductor and the value of gap is 0.674 eV using PBE potentials. The optical properties such as the dielectric function, refractive index, absorption coefficient, and real part of the optical conductivity, energy loss function and reflectivity have also been studied.

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