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Ab-initio Study of Electronic, Optical, Dynamic and Thermoelectric Properties of $CuSbX_2$ (X=S, Se) Compounds

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Abstract: In this work we investigate the electronic, optical, dynamic and thermoelectric properties of ternary copper-based Chalcogenides $CuSbX_2$ (X= S, Se) compounds. Calculations are based on density functional theory and the semi-classical Boltzmann theory. Computations have been carried out by using Quantum-Espresso (PWSCF) package and ab-initio pseudo-potential technique. To estimate the exchange-correlation functional various approximations were used, which among them GGA approximation led to better results. Density of state calculations indicates that $CuSbSe_2$ and $CuSbS_2$ compounds are semiconductors with a band gap of about 0.81 eV and 0.62 eV respectively. A lack of negative frequencies in the phonon dispersion curves of these compounds shows the stability of the compounds. The static refractive indices of $CuSbSe_2$ compound are 4.38, 3.66 and 3.30 calculated within GGA, GGA+U and GGAmBJ+U approximations respectively and plasmon frequencies obtained from the peak of the loss function is occurred at energies around 16eV.A trend of electrical conductivity behavior against temperature verify the semiconducting nature of the compounds which is in good agreement with electrical results.

Keywords: Ab-Initio, Density Functional Theory, Optical Properties, Thermodynamic Properties, Semiconductor.

1. INTRODUCTION

$CuSbX_2$ (X= S, Se) Compounds are crystalline in orthorhombic layer structures. The space group of these compounds is pnma62 [1]. Thermoelectric and transport properties of $CuSbSe_2$ and the doped compounds by Ti and Pb at low temperatures from 5 to 310 K including electrical conductivity, electrical resistance, hall coefficient and thermal conductivity have been experimentally explored by Lee and et al [2]. Ternary semiconductors Chalcogenides were synthesized by direct fusion, and the structural properties of $CuSbX_2$ (X= S, Se)

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compounds in a powder form and thin film were investigated by x-ray diffraction [3]. CuSbS2 compound is one of the important semiconductors with narrow band gap showing potential applications in various optoelectronic devices such as infrared detectors, and as an absorber material in solar cells [4, 5]. It has an indirect band gap and high absorption coefficient. In the past few decades, a large part of researches has been devoted to thermoelectric materials that directly convert heat to electricity. These materials are used in refrigerators and generators. Using density functional theory, thermoelectric properties of $CuSbS_2$ and $CuGaTe_2$have been theoretically studied by Vigo et al., [6]. These properties have been obtained by solving semi-classical Boltzmann equation and constant relaxation time approximation. In addition, the band structure of $CuSbS_2$ compound was calculated with augmented linearized plan wave method with full potential by using mBJ approximation, which has reported E_g=1.2eV[7]. There are no theoretical data to compare the electrical conductivity in terms of temperature of $CuSbX_2$ (X= S, Se), but electrical conductivity of $CuSbS_2$ has been investigated in terms of electrons and holes concentration.

2. THE METHOD OF CALCULATION

The bulk properties of $CuSbX_2$ (X= S, Se) compounds with an orthorhombic structural phase have been calculated within the density functional theory framework by using PWSCF computational code [8]. This package can be used as a pseudo-potential approach to describe the electron-ion interaction and to use the plane wave to develop the wave function and charge density [9,10]. In each cell of $CuSbX_2$ (X= S and Se) compound are 16 atoms (8 Cu atom, 4 Sb atom and 4 X atom in unit cell). For each composing element of these compounds, the types of pseudo-potentials, which are used, are norm conserving and consist of Cu.pbe-mt_fhi.UPF، Sb.pbe-mt_fhi.UPF ،Se.pbe-mt_fhi.UPFand S.pbe-mt_fhi.UPF. We have utilized GGA approach to find out the exchange-correlation functional. We reviewed and approved the accuracy of the pseudo-potentials, used by repeating part of the calculations with whole electronic and full potential Wien2K software [11]. This package uses augmented linearized plan wave method to solve quantum equations Kohn-Sham. After optimizing important computational parameters, cutoff energy 80 Ry, the number of grid points in the first brillouin zone for band structure calculations, $4\times6\times2$, for transport calculations, $8\times12\times4$, are obtained. Convergence in the self-consistent calculations in the orthorhombic phase of these compounds is reached with 26 cycles and 2×10^{-6} Ry accuracy. Phonon calculations have been carried out by using perturbation density functional theory that utilizes computational code QHA (Quasi Harmonic Approximation). The optical properties such as dielectric function and absorption coefficients have been calculated. Transport properties of these compounds are calculated in the semi-classical approach of Boltzmann and constant time relaxation approximation. In this approach, transport parameters such as Seebeck coefficient and electrical conductivity have been expressed in terms of derivatives of energy. Transport calculations are carried out by BoltzTrap code in which Fourier energy bands expansion is used to calculate energy bands derivations [12]. It should be explained that calculations were performed with various approximations, but the results were mentioned for one of them.

3. RESULTS

A. Electronic Properties

The density of states describes distribution of electrons in energy spectrum. One of the important results obtained from the density of states curves is the band gap of the compound. In Figures1 and 2, the total density of states and contribution of each of the elements of $CuSbX_2$ (X= S, Se) compounds are plotted by using GGA approximation. From Figure 1, it can be seen that the maximum peak of the conduction band in energy 3eV and 2.5eV areas occurs due to 3p orbital of Se and S atoms in $CuSbSe_2$ and $CuSbS_2$ compounds respectively. The maximum peak of valence band in -3.5 eV and -2eV occurs due to the 3d orbital of Cu atom in these compounds. Therefore, as it is shown in Figures1 and 2, the 3d orbital of Cu atom plays a significant role in the occurrence of the maximum peak of the valence band while its contribution in the conduction band is close to zero. By increasing the energy in the conduction band, the contribution of the orbital 4p of atom Se and 5p of atom Sb will be increased. In addition, the 3d orbital contribution of atom Cu is zero in the conduction band, which is a reflection of covalently bond Cu-Sb, Cu-Se and Cu-S in the $CuSbX_2$ (X=S, Se) compounds. The major contribution of 3d orbital of Cu atom located at the top of valance band and the major contribution in conduction band are for the p orbital of Se and Sb atoms, and with high probably, the first transition of existing electrons, which will occur between the electrons, are mentioned. The results of band gap of these compounds are shown in table 1. They have a good compatibility with other results obtained by GGA approximation.

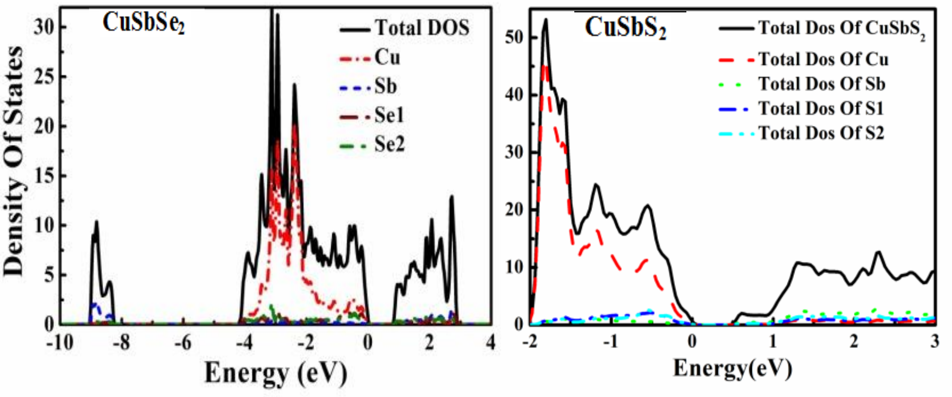

Fig.1. The total density of states for all constituting elements in $CuSbSe_2$ and $CuSbS_2$ compounds

Table1. The results for band gap of $CuSbX_2$ (X= S, Se) compounds with GGA approximation

	$CuSbSe_2$	$CuSbS_2$
GGA	0.81	0.62
Other work[6]	-	0.77
Experimental [6]	-	1.38

B. Optical properties

Optical properties play an important role to determine and classify materials take advantage of in solar cell systems. The study of optical properties is based on the calculation of absorption coefficients which can be directly reached from the dielectric function. Dielectric function is determined by the response of crystals to applied electromagnetic fields. This function is consisted of the two real,$\varepsilon_1(\omega)$, and the imaginary, $\varepsilon_2(\omega)$, parts $(\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega))$ the optical properties of these compounds are obtained with the complex dielectric function through equation (1)[13,14].

$$\varepsilon_2(\omega)=\frac{4\pi^2e^2}{m^2\omega^2}\sum\int\langle i|m|j\rangle^2 f_i(1-f_i)\delta(E_f-E_i-\omega)d^3k \qquad (1)$$

Where, M is the dipole matrix, i and j are the initial and final states, f_i is the Fermi distribution function for i^{th}mode and E_i is the electron energy in i^{th} mode. Real contribution of the dielectric function is obtained by using the imaginary part as well as the Kramers-Kronig relation in the form of the following equation (2) [15].

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} p \int_0^{\infty} \frac{\acute{\omega}\varepsilon_2(\acute{\omega})}{\acute{\omega}^2 - \omega^2} d\acute{\omega} \qquad (2)$$

The real part of the dielectric function at X, Y and Z directions have been investigated in Fig. 2 using GGA + U approximation.

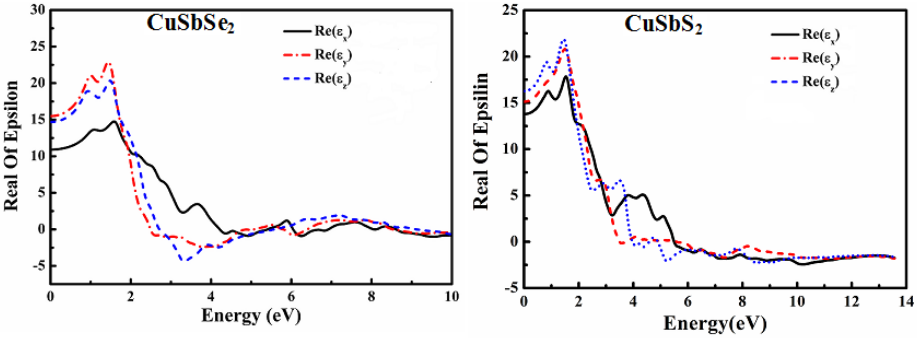

Fig.2. The real part of the dielectric function in X , Y , Z directions using GGA+U approximation for CuSbX$_2$ (X= S, Se) compound.

The roots of $\varepsilon_1(\omega)$ have the physical concept and in fact are a prerequisite for bulk Plasmon effects in material but adequate condition for them is the existence of energy loss. Also in the area with negative $\varepsilon_1(\omega)$ the wave's propagation will not be occurred while absorption and dissipation processes will happen. With calculating the real part of dielectric function in zero energy limits, the static refraction index of the system can be achieved [16].

$$n_0(\omega) = \sqrt{\varepsilon_1(0)} \qquad (3)$$

Table2. The real part of the dielectric function in zero energy in terms of eV in x ،y و z directions

	$\varepsilon_{1x}(0)$	$n_{0x}(\omega)$	$\varepsilon_{1y}(0)$	$n_{0y}(\omega)$	$\varepsilon_{1z}(0)$	$n_{0z}(\omega)$
CuSbSe$_2$	10.91	3.30	15.49	3.93	14.69	3.86
CuSbS$_2$	13.87	3.72	15.17	3.89	15.89	3.98

According to Fig. 2, it can be observed that the real part of the dielectric function reaches zero in several different energies and it can be one of the energies required for bulk Plasmon. In the X, Y and Z directions, the electromagnetic wave with energy higher than 4.17, 2.44 and 2.68eV respectively, is not propagated in CuSbSe$_2$ compound and Plasmon oscillations begin to start. The last amount of the energy which the wave can be propagated is equals to the maximum amount of energy loss.

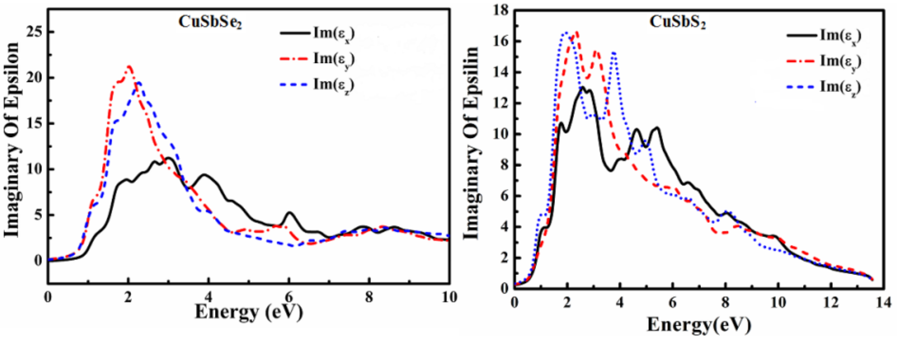

Fig.3. the imaginary part of the dielectric function in X, Y, Z directions

From Fig. 3 it can be observed that up to about 0.8eV, the imaginary part contains the slight changes which due to the absorption of the low- energy photons and lead to intra band transitions. But after the mentioned energy the imaginary part is suddenly increased representing the absorption through which the inter band transitions are occurred. The points shown in Fig. 4 indicate the required energy to transmit across the gap which represents the optical gap of the crystal. As it is observed the optical gap is respectively 0.81, 0.67, for CuSbSe$_2$ and CuSbS$_2$ compounds using GGA+U approximation that is in a good agreement with the results obtained from the electronic structure. Additional maximum points which are observed in the imaginary part of the dielectric function indicate the required energy for the following probable transitions.

B.1 Energy loss

Energy loss spectrum can be due to the mobility of mono-energy electron or due to the collective excitation of the valence electrons in a solid and its relation can be obtained by [15].

$$L(\omega) = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega)+\varepsilon_2^2(\omega)} \tag{4}$$

The main peak in the energy loss spectrum curve is the Plasmon peak, and the compound treats transparently at the higher frequencies. Several peaks may be existing for a substance. The maximum peak of the loss function in X, Y and Z directions occurs at energies of 16.70, 17.64 and 17.48 eV respectively for CuSbSe$_2$. These points are the energies at which the real part of the dielectric function reaches zero for the last time. It means that the compound contains the maximum level of energy loss (Fig. 4) in the mentioned energies and the wave is propagated for the waves with higher energy.

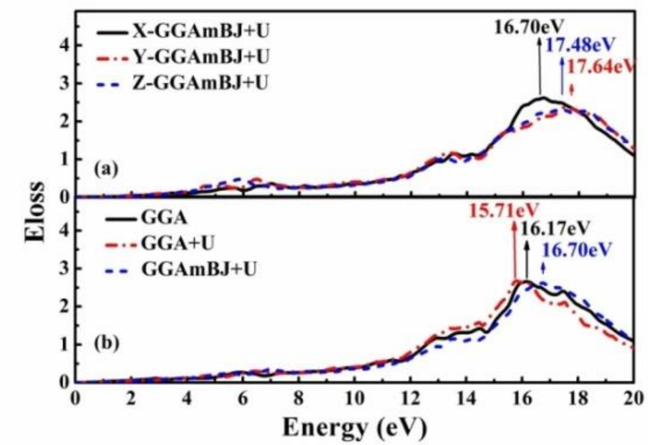

Fig.4. (a) Eloss Function in X,Y,Z directions using approximations GGAmBJ+U (b) ELoss Function in X direction using approximations GGA, GGA+U, GGAmBJ+U.

B.2 Refraction

The refraction index is an important physical parameter that depends on the mutual interactions of atomic microscopy. The refraction index can be defined based on the dielectric function in the form of Eq. 4[16].

$$n(\omega) = \sqrt{\frac{|\varepsilon(\omega)| + Re\varepsilon(\omega)}{2}} \tag{5}$$

The maximum refraction index of the compound in terms of energy in different directions with GGA+U approximation is shown in Fig. 5.

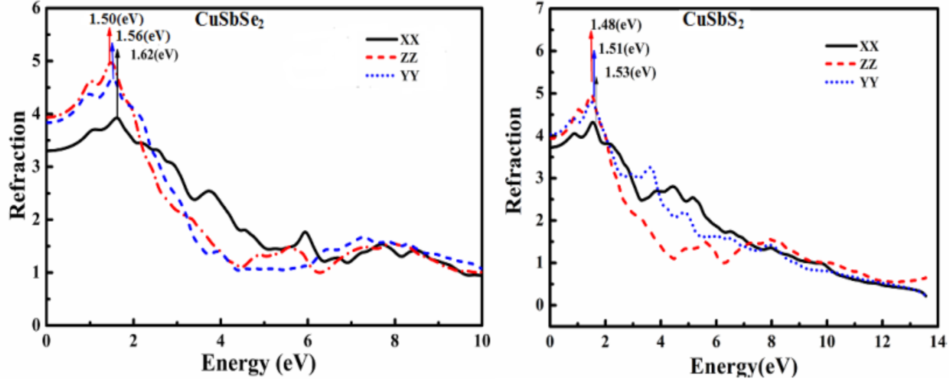

Fig.5. the refraction index in X, Y, Z directions using GGA+U approximation

C. Dynamic properties

A part of optical properties of materials is related to the response of ions to matter. Because the mass of ions is 10^3 times larger than that of electrons, the movements of ions are usually limited to the small fluctuations around the equilibrium positions in the lattice. Oscillating modes of lattice vibrations are called phonon modes. In crystals, the elastic waves are composed of phonon. Thermal vibrations in crystals are phonons, which thermally survive. Zero point energy of phonons is not zero, which meaning that the phonons are equivalent to a quantum oscillator. Therefore, the phonon frequencies must be positive; otherwise, crystal lattice will be unstable and the shape of crystal transforms spontaneously into a stable structure. Considering phonon properties, some of the thermal properties such as heat capacity, entropy, etc. can be calculated. A common method used to calculate phonon spectra is neutron scattering method. In addition, they are not easy to construct without blemish crystal and investigation of neutron scattering. Therefore, we investigate the phonon spectra of these compounds theoretically, which has not been studied yet. First, theoretically, by using Fourier transform, dynamical matrices become constant forces, and then the phonon spectra are calculated. Generally, phonons are divided into two acoustic and optical branches. The frequencies of acoustic branches reach zero in the Γ point. If the combinations have p atoms per unit cell, there are 3 acoustics modes and $3p-3$ optics modes. Phonon dispersion curve together with densities of states cure are plotted for $CuSbX_2$ (X= S, Se) compounds in the high direction symmetry phonon. Since each of these compounds has 16 basic atoms, we have totally 48 phonon modes of which 3 modes are acoustic and 45 ones are optic modes. One of the acoustic modes is longitudinal and two modes are transverses. Acoustic modes in $Y \rightarrow U$ directions are reduced from two branches to one branch, it means that in this direction, acoustic modes have double degeneracy. In Figures 6 and 7, we have plotted phonon dispersion and densities of states curvesfor $CuSbX_2$ (X= S, Se) compounds [17, 18].

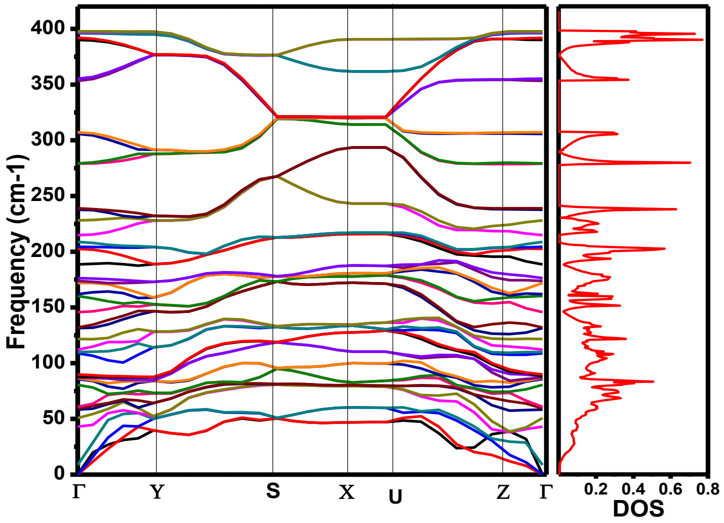

Fig.6. Phonon dispersion and density of states for CuSbSe$_2$compound

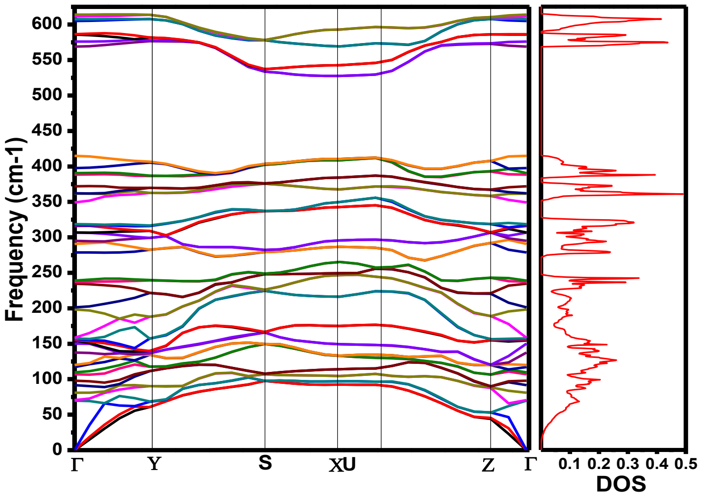

Fig.7. Phonon dispersion and density of states for CuSbS$_2$compound

It can be seen from both curves that all phonon frequencies are positive, which is consistent with experience and physics laws. This is a reason for the stability of these compounds in the orthorhombic phase. Phonon density of states curve of CuSbS$_2$ shows that this compound has a frequency gap about 100 cm^{-1}; therefore, it can be used as a mechanical filter.

D. Thermoelectric properties

Thermoelectric properties of ternary chalcogenides $CuSbX_2$ (X= S, Se), have been studied in this section. Low thermal conductivity of these materials is useful to produce thermoelectric generators with high efficiency [19, 20]. Thermoelectric generators, hence, have special importance because these materials have a little destructive effect on nature; they are clean and work without an additional power source. In Figure 8, the curves of electrical conductivity of $CuSbX_2$ (X= S, Se) compounds in constant relaxation time approximation in terms of temperature by using GGA approximation are plotted. These curves display that in the room temperature range (300K), electrical conductivity increases with increasing temperature; at temperature range 600K, they are almost constant and then they are reduced with increasing temperature. The reason for increasing electrical conductivity at 300K range is the thermal disturbances which survive between electrons and ions.

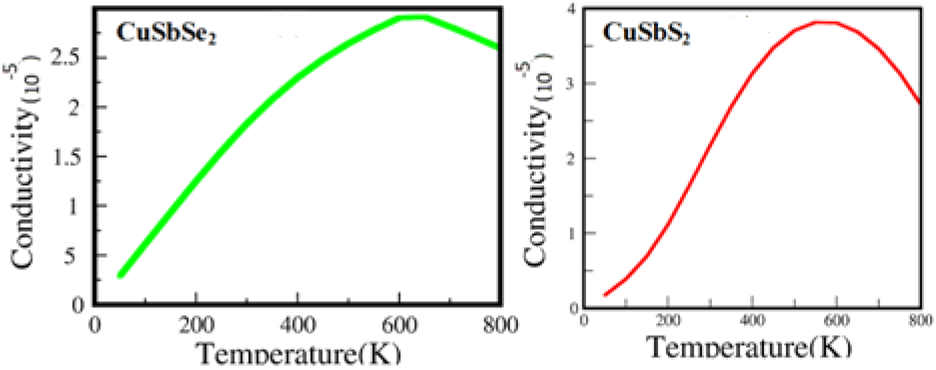

Fig.8. The curve of electrical conductivity in terms of temperature for $CuSbSe_2$ and $CuSbS_2$ compounds

4. CONCLUSIONS

In this paper, we have considered the electronic, optical dynamic, and thermoelectric properties of bulk state of ternary copper-based Chalcogenides $CuSbX_2$ (X= S, Se) in orthorhombic phase. Calculations have been carried out using ab-initio pseudo-potential method and GGA approximation with PWSCF package. The results of electronic structure point out these compounds are semiconductors, and the result of phonon dispersion curve show the stability of these compounds. $CuSbS_2$ Compound has a frequency gap about $100cm^{-1}$; therefore, it can be utilized as a mechanical filter. The optical gap is respectively 0.81, 0.67, for $CuSbSe_2$ and $CuSbS_2$ compounds using GGA+U approximation that is in a good agreement with the results obtained from the electronic structure. At the room temperature range (300K), electrical conductivity increases with increasing temperature; whereas, at the temperature range of 600K, it is almost constant, and then it is reduced with increasing temperature. The reason for increasing electrical conductivity at 300K range is the thermal disturbances which exist between electrons and ions.

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