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DFT calculations of the main optical constants of the $Cu_2ZnSnSe_xS_{4-x}$ system as high-efficiency potential candidates for solar cells

Nematov Dilshod
Laboratory for Research on Renewable Energy Sources, Physical-Technical Institute of the National Academy of Sciences of Tajikistan, Dushanbe, Tajikistan

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ABSTRACT

In the present work, using quantum-chemical calculations in the framework of density functional theory (DFT), we study the optical properties of semiconductor nanocrystals of kesterite Cu_2ZnSnS_4 doped with Se. Using the WIEN2k package, the concentration dependences of the optical characteristics of nanocrystals of the $Cu_2ZnSnSe_xS_{4-x}$ system (x = 0, 1, 2, 3, 4) were calculated. It is shown that doping with Se at the S position leads to a noticeable improvement in the photo absorbing properties of these nanocrystals, as well as their photoconductivity in the IR range. The calculated absorption and extinction spectra of the materials under study, are compared with experimental data known from the literature. The data obtained will significantly enrich the existing knowledge about the materials under study and will help expand the scope of these compounds in optoelectronic devices, especially in solar cells and other devices that convert solar energy into electricity.

Corresponding Author:

Nematov Dilshod
Laboratory for Research on Renewable Energy Sources
Physical-Technical Institute of the National Academy of Sciences of Tajikistan
Aini Ave. 299/1, 734063, Dushanbe, Tajikistan
Email: dilnem@mail.ru

1. INTRODUCTION

Increasing the use of renewable energy and conserving the environment are gaining popularity across the world. To maintain the sustainable development of life, governments, research institutions, and businesses are addressing the issues posed by a lack of energy supplies. It is commonly recognized that the best method to tackle environmental concerns is to employ renewable energy sources and innovative energy-efficient materials [1]. Based on this, the developed countries of the world, especially the countries of Europe, from year to year increase their investments in this area, so that scientists and engineers of the world as soon as possible develop modern means and new weapons to combat atmospheric pollution and achieve sustainable development of technologies and green energy. The very idea of developing new energy-efficient materials and switching to renewable energy sources is in line with the UN strategy to prevent global problems (paragraphs 7 and 13 of the sustainable development strategy) for the period up to 2030. Solar energy is considered to be the most economical and efficient renewable energy source available. It is inexhaustible and "environmentally friendly," does not produce waste and additional heat load on the environment when used [1], [2].

Recently, photovoltaic (PV) systems have received a lot of attention due to their advantage over other renewable energy sources due to the ability to directly convert solar energy into electricity and avoiding

system wear caused by mechanical movement (since photovoltaic systems do not necessarily contain moving parts). Therefore, solar power plants can operate continuously without maintenance for longer than devices using other power generation technologies. On the other hand, the theoretical conversion efficiency of photovoltaic systems is relatively higher than that of other generators [2].

Currently, three thin-film materials are widely used in the industrial production of solar cells: single-crystal and polycrystalline silicon (Si), cadmium telluride (CdTe) and copper-indium-gallium selenide/sulfide $CuIn_xGa_{1-x}S(Se)_2$ (CIGS), among which CIGS has achieved the highest efficiency (20.8% in laboratory devices) and can compete with polycrystalline silicon [3], [4]. Thin-film silicon-based solar cells have been relatively underdeveloped due to low efficiency and instability as a result of the Stabler-Vronsky effect [2]. The other two thin-film technologies suffer from serious manufacturing toxicity issues, soaring material costs and/or low natural abundance of raw materials, which are predicted to severely limit the production, mass deployment and economic sustainability of these solar cells [5]–[12]. Indium (In) is a rare element and may run out in the next 10-20 years, while its price has been rising rapidly in recent years [12] . The use of toxic cadmium (Cd) has hindered the mass production and adoption of CdTe solar cells due to environmental aspect concerns [13]. Thus, intensive research is needed to develop alternative thin-film solar-absorbing materials, including naturally occurring, inexpensive and non-toxic elements that can be incorporated into high-performance devices, be economically competitive with traditional energy sources. Cu_2SnS_3 (CTS), Cu_2ZnSnS_4 (CZTS), and $Cu_2ZnSnSe_4$ (CZTSe) compounds are being investigated as a potential alternative to the widely used CdTe and CIGS ($CuInGaSe_2$) solar absorbers [14]. On the other hand, it will be very interesting to synthesize and study their shifted structure, since these semiconductors attract attention as photon-absorbing layers of thin-film solar cells due to their direct band gap of 1.0–1.5 eV, high optical absorption coefficient ($>10^4$ cm^{-1}) and p-type conductivity [15]–[18]. In addition, they consist of cheap and environmentally friendly elements. The reserves of copper (Cu), zinc (Zn), tin (Sn) and sulfur (S) in the earth's crust are 68 ppm, 79 ppm, 2.2 ppm and 420 ppm, respectively, compared to 0.16 ppm (In), 0.15 ppm (Cd) and 0.001 ppm (Te) [19]. Calculations on the photon balance of Shockley-Keisser estimated the theoretical conversion efficiency of CZTS single-junction solar cells at 32.2% [20]. Over the past few years, the efficiency of solar cells based on CTS and CZTS has reached a record value of 4.63% and 9.2%, respectively [21], [22].

Every year, the number of publications devoted to these materials and the number of scientific groups that use various techniques to create and study thin layers of these materials is increasing. However, the study of the fundamental properties of these compounds, especially their optical and elastic properties, remains at a rather low level, which hinders a further increase in the efficiency of structures based on them. It is important to note that the modeling of physical phenomena has long been an important area of interdisciplinary research, and quantum-chemical studies of nanoscale structures based on semiconductor materials, in particular kesterites, are of great interest in connection with the creation of reliable optoelectronic devices based on them. In contrast to a bulk material, in which an indirect band gap prevents effective photon generation, kesterite nanocrystals exhibit relatively intense radiation [23] in the red and near infrared (IR) ranges. As mentioned above, a great advantage of using nanocrystals and thin films as key elements in the creation of radiation sources is the ability to control their electron-optical properties, which can be done, for example, by changing the material matrix, the size of nanoclusters, introducing impurities, atoms, etc. In this regard, much attention is currently paid to the theoretical and experimental study of the optoelectronic structure of kesterite nanocrystals. One of the most powerful theoretical approaches to studying the band structure and optical properties of not only nanocrystals but also bulk systems is the density functional theory (DFT) method. On the other hand, this method is currently one of the most universal first-principles (ab initio) methods for calculating the electronic structure, optical properties, elasticity, and various other characteristics of multiparticle systems and is used in solid state physics and quantum chemistry. The description of a multielectron system within the framework of DFT is carried out not with the help of the wave function, which would cause a very large dimension of the problem (at least equal to 3N values of the coordinates of N particles), but with the help of the electron density function, a function of only three spatial coordinates, which leads to a significant simplification tasks. It turns out that the most important properties of a system of interacting particles can be expressed using the electron density functional, in particular, according to the Hohenberg–Kohn theorems [24], [25] which provide the theoretical basis for the DFT method, such a functional is the energy of the ground state of the system.

In condensed matter physics, especially for accurate DFT calculations of the structural, electronic, and optical properties of nanomaterials, software packages based on the linearized augmented plane wave method are very effective. One such software package is WIEN2k [26], which has been widely implemented in recent years for high-precision modeling of the properties of solid materials using distributed multiprocessor computing based on technologies such as MPI and CUDA that support standard parallel programming technologies. In this work, using the WIEN2k package, we calculated the optical properties of

both pure and undoped kesterites of the Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ systems and their displaced structures ($Cu_2ZnSn[S/Se]_4$) depending on the ratio of sulfur and selenium. In a recent work, the geometry and electronic band structure of the studied materials were studied using ab initio mBJ-calculations [27]. However, the optical properties of these nanocrystals, especially with the use of the mBJ exchange-correlation functional, have not been previously studied.

2. METHOD

First-principles quantum chemical calculations within the framework of DFT were performed on the basis of our optimized orthorhombic lattices of pure and selenium-doped Cu_2ZnSnS_4 from a previous work [27], for which the electronic properties were also studied taking into account spin-polarized and spin-orbital effects. Thus, at the first stage, the structures were optimized in order to determine the equilibrium positions of atoms from the forces acting on the atoms. Calculations of the geometric structure and optoelectronic properties of Cu_2ZnSnS_4 doped with selenium after geometry optimization were performed using a full-potential plane wave packet and a local orbit WIEN2k, where the exchange-correlation effects were estimated by the modified TB-mBJ potential [28]. Numerous works state that this exchange-correlation functional gives an experimentally comparable estimate of the band gap and parameters of optical properties [29]–[34] compared to other known approximations. The scheme and stages of mBJ calculations for evaluating the electronic and optical properties of materials are shown in [35]. The optimal plane wave cutoff value K_{max} was chosen to be 6.0 $Ry^{1/2}$ after performing convergence tests. A uniform 1×1×1 k-point grid was used for all calculations. The Kohn-Sham equations were solved on the basis of LAPW. Kesterite crystals with a tetragonal syngony (symmetry group I-4) were chosen as the structures under study. For calculations of optical properties, the muffin-tin radii for $Cu_2ZnSnSe_xS_{4-x}$ (x = 0, 1, 2, 3, 4) were 2.31, 2.39, 2.50, 1.96 and 2.20 a.u. for Cu, Zn, Sn, S, and Se, respectively.

3. RESULTS AND DISCUSSION

All solid materials have the ability to absorb, transmit, and reflect processes that can be quantified and modeled at the macroscopic and microscopic levels. At the microscopic (quantum-mechanical) level in bulk nanostructures, the complex dielectric function is strongly related to the band structure. The optical characteristics of kesterite are calculated directly from the complex dielectric function $\varepsilon(\omega)$, which contains the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts as frequency dependent functions. In Figure 1 shows the $\varepsilon_2$spectra spectra of for $Cu_2ZnSnSe_xS_{4-x}$ system (x = 0, 1, 2, 3, 4) obtained from DFT calculations. The method for DFT-calculating the imaginary part of the permittivity tensor $\varepsilon_2(\omega)$ is shown in [36].

The $\varepsilon_2(\omega)$ spectrum of nanocrystals of the $Cu_2ZnSn[S_{1-x}Se_x]_4$ system is dominated by three peaks located at 1.9, 4.7, and 7.2 eV, respectively. These peaks can explain the results of calculations of the total density of electronic states published in our previous work [27], in which the reflectivity of these nanocrystals was also estimated. In this case, the peak at 1.9 eV, determined from calculations of the total and partial densities of electronic states, represents transitions from the Cu-3d/S-3p states to the Sn-5s/S-3p band. They can also be characterized by the features of the crystal structure of the materials under study [37]–[40]. The peak at 4.7 eV refers to transitions from the Cu-3d/S-3p states to the Sn-5p/S-3p states or transitions from the hybridization of the Cu-3d, Sn-5p and S-3p states to the antibonding Sn-5s/C-3p states. The peak at 7.2 eV is associated with transitions from the hybridization of the Cu-3d, Sn-5p, and S-3p states to the antibonding Sn-5p/S-3p states. The $\varepsilon_2(\omega)$ spectrum of $Cu_2ZnSnSe_4$ exhibits a shift of the peaks towards low energies due to a slightly smaller band gap than that of Cu_2ZnSnS_4. Figures 2-5 respectively show the calculated spectra of extinction $k(\omega)$, absorption $\alpha(\omega)$ and energy loss $L(\omega)$, as well as the real and imaginary parts of the photoconductivity $\sigma(\omega)$.

Usually, when light propagates in a medium, dissipation (weakening) of a light beam, the cause of which is the combined action of the processes of absorption and scattering of light during its propagation in a substance [41], [42]. This is an optical property of a material related to the refractive index of the material. The measure of light attenuation is the light extinction coefficient (k). Positive value of k shows that the absorption is going to be take place, while k=0 shows that the light travels straight through the material. However, if scattering plays no role compared to absorption, then the extinction coefficient becomes the same as the absorption coefficient. On the other hand, the extinction coefficient of materials means how actively a substance absorbs light with a certain wavelength [41], [42].

The absorption coefficient (α) is one of the most important parameters for materials used as absorbing layers in photovoltaic cells. The maximum absorption of the studied materials is in the ultraviolet region. On the other hand, absorption coefficient shows the depth of penetration of light of a certain wavelength before absorption and depends on both the incident light and the internal properties of the material [43], [44]. The rate of absorption of light is proportional to the intensity (the flux of photons) for a

given wavelength. That is, light that is transmitted through the absorbing material is attenuated by a significant amount as it passes through; in other words, as light passes through the material the flux of photons is diminished by the fact that some are absorbed on the way through. Therefore, the number of photons that reach a certain point in the semiconductor depends on the wavelength of the photon and the distance from the surface. Typically, absorption is selective selective in nature, i.e., light of different wavelengths is absorbed differently. Since the wavelength determines the color of light, therefore, rays of different colors are absorbed differently in a given substance. A recent study shows that as the wavelength of light increases, there is a corresponding increase in penetration depth [45]. In this case, transparent bodies are bodies that give a small absorption of light of all wavelengths related to the interval of visible rays, and the dependence of α on λ is a curve with a number of maxima, which, in turn, are absorption bands of light by a substance for a certain wavelength interval. According to Figure 3, the absorptivity of the studied systems increases with an increase in the selenium concentration; therefore, for $Cu_2ZnSnSe_4$, maximum absorption is observed in the IR region and covers the maximum range of the solar spectrum. The maximum extinction and absorption coefficients are in the same energy range, which agrees with the dispersion theory [46].

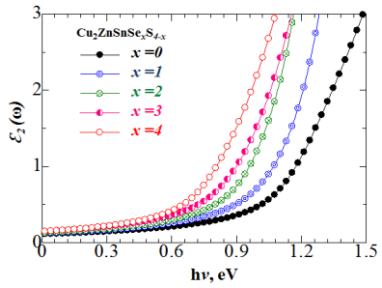

Figure 1. Imaginary part of the dielectric function for kesterites of the $Cu_2ZnSnSe_xS_{4-x}$ (x = 0, 1, 2, 3, 4) system, calculated using the mBJ approximations

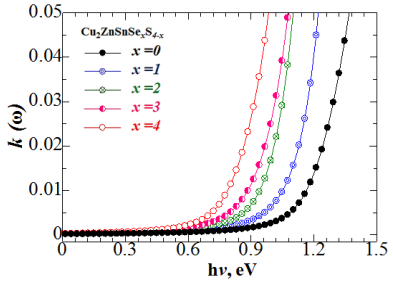

Figure 2. Dependences of the extinction coefficient of nanocrystals of the $Cu_2ZnSnSe_xS_{4-x}$ (x = 0, 1, 2, 3, 4) family on the photon energy

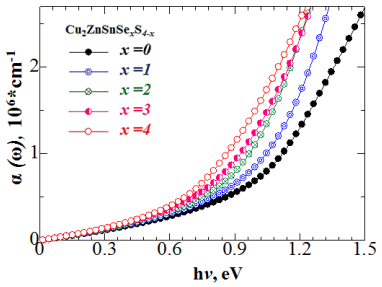

Figure 3. Dependences of the absorption coefficient on the photon energy for the model structures of the $Cu_2ZnSnSe_xS_{4-x}$ (x = 0, 1, 2, 3, 4) system

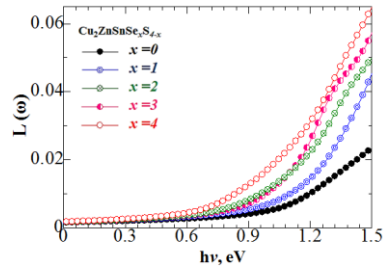

Figure 4. Calculated energy loss spectrum for the $Cu_2ZnSnSe_xS_{4-x}$ (x = 0, 1, 2, 3, 4) system depending on the photon energy

Figures 5(a) and 5(b) shows the real and imaginary parts of the photoconductivity of independent nanocrystals of the system under study, calculated by the DFT method. Optical conductivity is the property of a material that couples current to electric field for frequency. In this sense, this linear response function is a generalization of electrical conductivity, which usually switches in the static limit, that is, for a time-independent (or rather slowly changing) electrical region. While static electrical conductivity is vanishingly small in insulators (for example, diamond or porcelain), optical conductivity always remains finite in some frequency intervals (higher optical gap in the case of insulators); the total optical weight can be derived from the summation rules. Optical propagation propagation with dielectric frequency, a generalization of permittivity to arbitrary frequencies. Figure 5 shows that the doping of Se in the S-position leads to a noticeable improvement in the photoconductivity of the studied materials in the IR range.

The shape of the curves of the extinction coefficient k(ω) shown in Figure 2 is in good agreement with the maxima of the imaginary part of the permittivity $\varepsilon_2(\omega)$. Calculations of the absorption coefficient show that, as always, the absorption maximum is in the ultraviolet region. For solar cells, the energy range of

visible and IR light is important, where the average order of magnitude of α exceeds 10^4 cm^{-1}, while the materials under study have a higher absorption coefficient, which is remarkably suitable for absorbing layers of thin-film solar cells. This result agrees with the values obtained in experiments [47]. It can be seen from the obtained results that with an increase in the selenium concentration in the system, the absorption in this region increases, which is associated with a larger imaginary part of the dielectric function $\varepsilon_2(\omega)$ of Cu_2ZnSnS_4 compared to $Cu_2ZnSnSe_4$. In the region of intrinsic absorption, the absorption edge of Cu_2ZnSnS_4 is shifted to the blue region compared to the absorption edge of $Cu_2ZnSnSe_4$, in accordance with a slightly larger band gap. The calculated values of the optical band gap obtained using the Kubelka - Munk functions $((\alpha h\nu)^{1/2}$, where α is the absorption coefficient) depending on the photon energy (hν), also confirmed the decrease in the band gap of the $Cu_2ZnSnSe_xS_{4-x}$ (x = 0, 1, 2, 3, 4) system with increasing selenium content. The optical band gap in our calculations decreases from 1.3 to 0.95 eV with the gradual replacement of Se by S, these values are consistent with the electronic band gaps recorded in them of about 1.0 eV for $Cu_2ZnSnSe_4$ and 1.44 eV for Cu_2ZnSnS_4 [48], [49]. Table 1 shows the calculated average values of the static (ε_0) and high-frequency (ε_∞) permittivity for the materials under study and compared with the literature data.

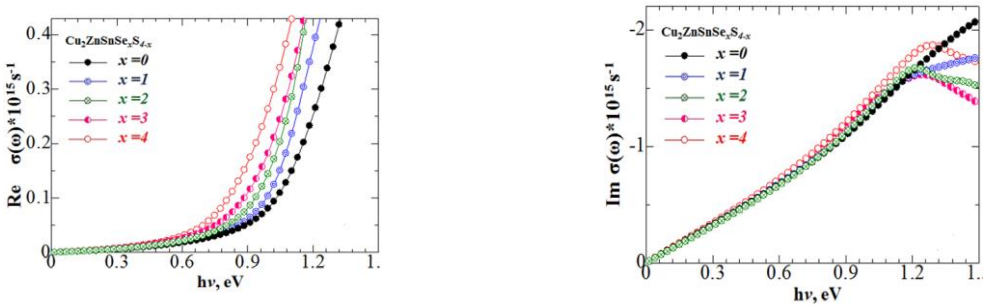

Figure 5. Spectra of the (a) real part and (b) imaginary part of the optical conductivity of the $Cu_2ZnSnSe_xS_{4-x}$ (x = 0, 1, 2, 3, 4) system as a function of photon energy

Table 1. Comparison of the results of calculations of ε_0 and ε_∞ with literature data

$Cu_2ZnSnSe_xS_{4-x}$	ε_0		ε_∞	
	This work	In literature	This work	In literature
$x = 0.00$	9.83	10.4^e, 8.24^f	8.30	7.9^e
$x = 0.25$	9.52	9.5^e, 7.89^f	7.50	7.5^e
$x = 0.50$	9.35	9.4^e, 7.51^f	7.21	7.2^e
$x = 0.75$	9.11	9.2^e, 7.28^f	6.73	6.8^e
$x = 1.00$	8.67	9.0^e, 6.75^f	6.52	6.5^e

[e]Ref. 50 [f]Ref. 51

According to Table 1, our results are somewhat lower than those obtained by the HSE06 method in [50], however, all obtained values of ε_0 are larger than the results given in [51]–[54]. It can be seen that the calculated permittivities decrease when selenium is replaced with sulfur, which indicates an inverse relationship between the energy gap and the dielectric response. Thus, the S/Se ratio can be used to adjust the optimal band gap of the $Cu_2ZnSnSe_xS_{4-x}$ (x = 0, 1, 2, 3, 4) system.

4. CONCLUSION

In this work, the optical properties of the $Cu_2ZnSnSe_xS_{4-x}$ (x = 0, 1, 2, 3, 4) system on the basis of first-principles calculations using the mBJ exchange-correlation potential were studied. The main results obtained indicate that the absorption of solar radiation by these materials when used in solar cells is associated with electronic transitions from the antibonding states of Cu-3d/S-3p to the antibonding states of Sn-5s/S-3p. According to the results, the permittivity curves and the main optical spectra of all members of the $Cu_2ZnSnSe_xS_{4-x}$ (x = 0, 1, 2, 3, 4) family have fairly similar features in the IR region ofн radiation, despite the different composition and structure. It was found that the optical absorption coefficient, which is proportional to the imaginary part of the permittivity, is quite large in the IR and visible light energy range (>10^4 cm^{-1}). It became known that all nanocrystals of the $Cu_2ZnSnSe_xS_{4-x}$ (x = 0, 1, 2, 3, 4) system are transparent in the high-energy region, which does not affect the absorption of visible light. In accordance with the above properties, Se-doped Cu_2ZnSnS_4 kesterites are promising materials for use as an absorber in thin-film solar cells.

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BIOGRAPHIES OF AUTHORS

Dilshod Nematov has been working at the S. U. Umarov Physical-Technical Institute of the National Academy of Sciences of Tajikistan since 2021, before that he worked as a senior lecturer in the Department of Physics at the Tajik Technical University. Currently, he is a Senior Research Fellow at the Center for Research and Use of Renewable Energy Sources of the National Academy of Sciences of Tajikistan. He is the editor of the journal "SCI-ARTICLE" on physics, energy, nanotechnology and materials science. He received a specialist degree from the Tajik National University and then a PhD in Engineering from the Tajik Technical University, Tajikistan. He has done research, provided industry advice, and published over 40 publications in his area of expertise. He can be contacted at e-mail: dilnem@mail.ru.