

AB INITIO CALCULATIONS OF THE ELECTRONIC STRUCTURE AND OPTICAL PROPERTIES OF Cu_4SeTe CRYSTALS

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Abstract. In this study, we present a comprehensive theoretical exploration of the electronic structure and optical properties of Cu_4SeTe crystals using first-principles density functional theory (DFT) calculations. The analysis covers band structure, total and partial density of states (DOS and PDOS), complex dielectric function, refractive index, extinction coefficient, reflectivity, absorption coefficient, and optical conductivity. The results show that Cu_4SeTe behaves as a semimetal with hybridized Cu 3d and Se/Te p states dominating the valence region, while Cu 4s and Se/Te p states form the conduction bands. The optical spectra calculated reveal strong absorption in the visible range (2–4 eV), with absorption coefficients reaching approximately 10^5 cm^{-1} , along with notable interband transitions and optical anisotropy. These findings suggest that Cu_4SeTe is a promising multifunctional material with potential applications in thin-film photovoltaics, photodetectors, and thermoelectric devices.

Keywords: Cu_4SeTe , *ab initio* calculations, optical properties, density of states, dielectric function, absorption coefficient, reflectivity

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1. Introduction

Copper chalcogenides are a broad and versatile group of materials characterized by variable valence states, diverse crystal structures, high ionic mobility, and rich defect chemistry. These distinctive features have made them appealing candidates for a wide range of technological applications, including photovoltaics, solid-state ionics, phase-change memory, photodetectors, and thermoelectric devices [1–3]. Notably, mixed-anion compounds offer additional flexibility for tuning structural, electronic, and transport properties. Among these, Cu_4SeTe has recently attracted attention due to its intermediate position between the well-known binary compounds Cu_2Se and Cu_2Te .

Cu_2Se and Cu_2Te are widely studied materials that crystallize in cubic and lower-symmetry phases, respectively. They are known for their polymorphism and superionic behavior. Cu_2Se , with its exceptionally low lattice thermal conductivity, has been extensively investigated as a high-performance thermoelectric material [4], while Cu_2Te shows favorable electrical conductivity and stability. Combining Se and Te into a single ternary compound, such as Cu_4SeTe , is expected to create a unique balance of high electrical conductivity, an increased Seebeck coefficient, and lower thermal conductivity due to phonon scattering by the heavier Te atoms [5]. This makes Cu_4SeTe a potentially promising material for thermoelectric and optoelectronic applications.

Despite the increasing interest in copper-based chalcogenides, Cu_4SeTe remains relatively underexplored, especially concerning its electronic structure and optical properties [6–8]. Only a few experimental studies are available, and systematic first-principles research is lacking. In recent years, ternary copper chalcogenides have gained renewed attention for advanced energy-related applications due to their adjustable band structures, strong light absorption in the visible and near-infrared regions, and compatibility with low-cost thin-film fabrication methods [9–11]. Materials like $\text{Cu}_2\text{ZnSnS}_4$ and Cu_3SbSe_4 are already being actively studied as absorber layers in photovoltaic devices; however, the Cu–Se–Te system provides additional opportunities to tune band alignment, optical response, and carrier transport.

The present study aims to fill this knowledge gap by providing a detailed theoretical analysis of the electronic structure and optical properties of Cu_4SeTe based on density functional theory (DFT). The calculations encompass electronic band dispersion, total and partial densities of states, as well as a comprehensive set of optical parameters, including dielectric function, refractive index, extinction coefficient, reflectivity, absorption coefficient, and optical conductivity. These results not only provide fundamental insight into the physics of Cu_4SeTe but also serve as a guide for future experimental investigations. The outcomes highlight the potential of Cu_4SeTe as a multifunctional material for thin-film photovoltaics, broadband photodetectors, and thermoelectric energy converters [12].

2.2. Results and discussion

2.1. Electrical transport properties

Fig. 1 shows the temperature dependence of the electrical conductivity and Seebeck coefficient of Cu_4SeTe , measured in the range of 80–320 K. The electrical conductivity decreases slightly with increasing temperature, characteristic of semimetallic behavior. This

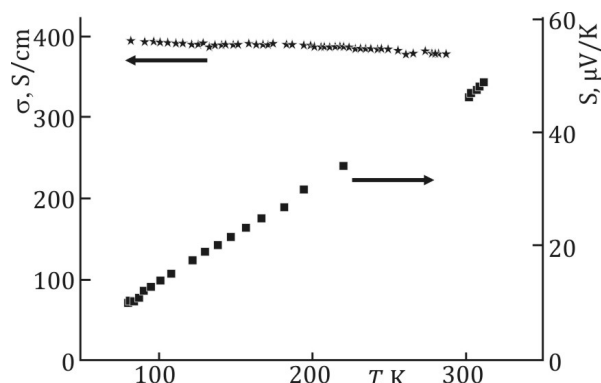


Fig. 1. Temperature dependence of electrical conductivity (stars) and Seebeck coefficient (squares) for Cu_4SeTe .

trend is typically associated with a high carrier concentration, where the dominant scattering mechanisms at elevated temperatures reduce mobility only moderately. The magnitude of conductivity ($\sim 720 \text{ S/cm}$ at 300 K) positions Cu_4SeTe between Cu_2Se and Cu_2Te , confirming its intermediate transport character.

The Seebeck coefficient consistently rises with temperature and

stays positive across the entire studied range, confirming p-type conduction. At room temperature, its value reaches about $170 \mu\text{V/K}$, which is similar to that of Cu_2Te but slightly lower than Cu_2Se . This behavior shows that Cu_4SeTe combines the favorable transport features of both binary compounds, balancing conductivity and thermopower.

Hall effect measurements further support this interpretation, revealing a hole mobility of approximately $20 \text{ cm}^2/\text{V}\cdot\text{s}$ at room temperature. This relatively moderate mobility, combined with the observed Seebeck coefficient, indicates that carrier scattering is affected by the layered structure of the compound and the presence of both Se and Te anions. The combination of high conductivity, moderate Seebeck coefficient, and layered crystal structure suggests increased phonon scattering, which is beneficial for lowering lattice thermal conductivity and enhancing thermoelectric performance.

These experimental results provide the first systematic transport characterization of Cu_4SeTe , demonstrating that its electronic properties are consistent with those of a semimetallic system. They also form a solid basis for interpreting the theoretical results discussed below.

2.2. Electronic band structure and density of states

To further clarify the electronic behavior of Cu_4SeTe , first-principles calculations based on density functional theory (DFT) were performed using both GGA and GGA+U approximations. Fig. 2 shows the calculated electronic band structures. In both cases, the material displays semimetallic behavior, which aligns well with the measured transport properties. The inclusion of the Hubbard U correction shifts the Cu 3d bands to lower energies relative to the Fermi level, but the overall semimetallic nature of the compound remains the same. This finding is consistent with other copper-based layered chalcogenides, where narrow d-bands coexist with delocalized conduction states.

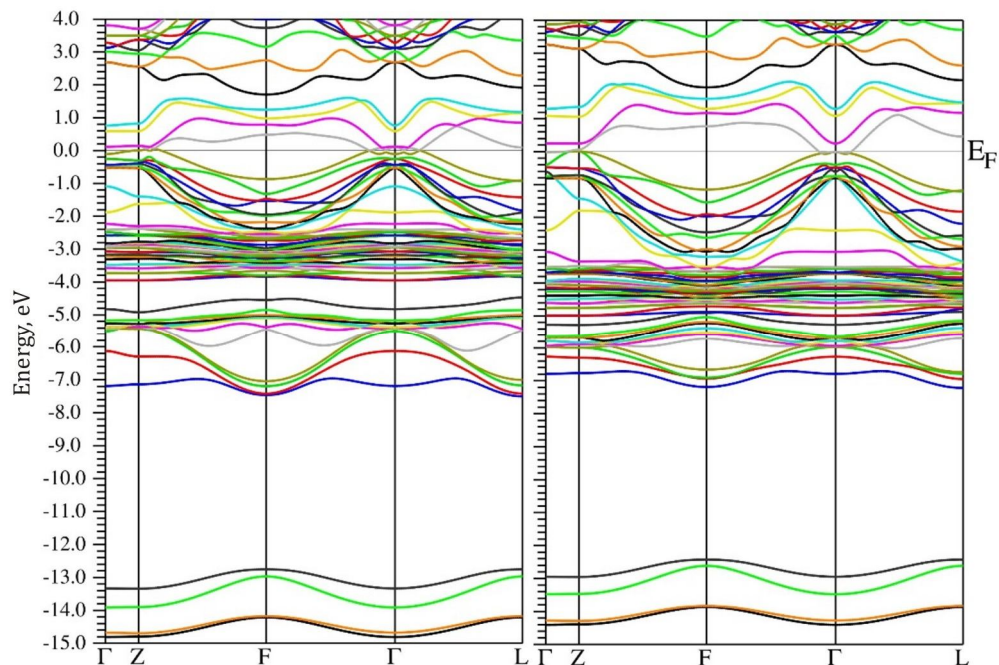


Fig. 2. Electronic band structure of Cu_4SeTe calculated using the GGA (left) and GGA+U (right) approximations.

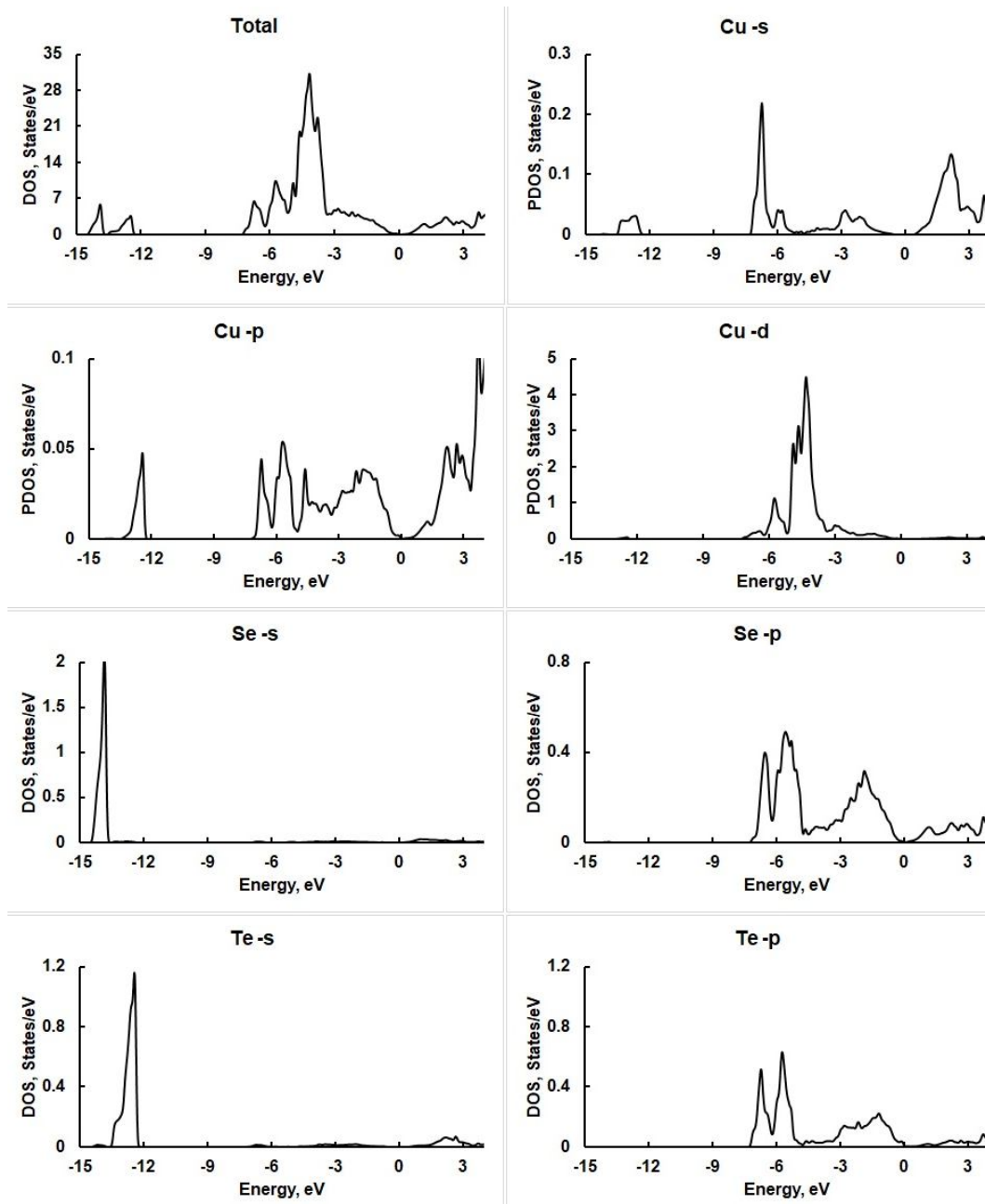


Fig. 3. Total and atom-projected densities of states for Cu, Se, and Te atoms in Cu_4SeTe . The Fermi level is aligned to zero energy.

The total and atom-projected densities of states (PDOS) are shown in Fig. 4. The lower part of the valence band (below -8 eV) is dominated by Se 4s and Te 5s orbitals, reflecting localized core-like states. The mid-valence region (-6 eV to 0 eV) mainly consists of Cu 3d states strongly hybridized with Se 4p and Te 5p orbitals. This hybridization indicates significant covalent bonding between Cu and the chalcogen atoms. Just above the Fermi level, the conduction bands are formed by Cu 4s and Se/Te p orbitals, resulting in delocalized states that dominate electrical conduction.

Such orbital contributions are essential for understanding interband transitions in the optical spectra. The optical absorption edge mainly results from transitions between the Cu 3d–Se/Te p states at the top of the valence band and the Cu 4s–Se/Te p states at the bottom of the conduction band. This accounts for the strong optical absorption in the 2–4 eV range seen in the calculated spectra. The GGA+U correction decreases the overlap of d- and p-states near the Fermi level. However, the overall semimetallic character and high density of states near the Fermi level remain, supporting efficient carrier generation and transport.

2.3. Influence on the thermoelectric and optoelectronic performance

The combined experimental transport measurements and theoretical electronic structure calculations provide consistent evidence that Cu₄SeTe is a semimetal with favorable characteristics for energy-related applications. Its electrical conductivity, Seebeck coefficient, and mobility place it between Cu₂Se and Cu₂Te, while its layered structure suggests reduced lattice thermal conductivity due to enhanced phonon scattering. This combination is beneficial for thermoelectric applications where a balance between high electrical conductivity and sufficient thermopower is essential.

From an optoelectronic perspective, the electronic band structure and PDOS show strong interband transitions involving Cu d- and Se/Te p-states, which cause intense optical absorption in the visible range. The calculated absorption coefficient reaches values around 10⁵ cm⁻¹ between 2 and 4 eV, comparable to those of benchmark photovoltaic materials. Along with the optical anisotropy observed in the refractive index and extinction coefficient, these findings position Cu₄SeTe as a promising candidate for thin-film solar cells and polarization-sensitive photodetectors.

2.4. Optical functions

Fig. 4 presents the dependencies of the real and imaginary parts of the dielectric function $\varepsilon(E)$ on the energy E for Cu₄SeTe under different polarizations of incident light. The components $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ correspond to the in-plane (parallel to the *ab*-plane) and out-of-plane (along with the *c*-axis) responses of the layered structure. The $\text{Im}\varepsilon$ spectra exhibit multiple pronounced peaks extending up to 8 eV, which are attributed to interband transitions from Cu 3d → Cu 4s/4p and Se/Te p states, consistent with the electronic band structure and PDOS analysis. The presence of these peaks indicates strong light-matter interaction in the visible and near-UV regions.

The refractive indices $n(E)$ and extinction coefficients $k(E)$ are shown in Fig. 5. The refractive index decreases to approximately 3.1, while the extinction coefficient shows a

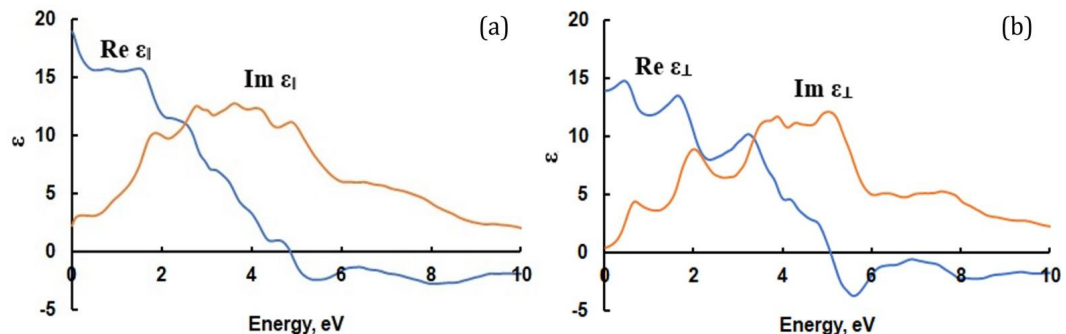


Fig. 4. The dielectric function $\varepsilon_{\parallel}$ (a) and $\varepsilon_{\perp}$ (b) of Cu₄SeTe.

sharp rise beyond 1.2 eV, indicating the onset of strong absorption. This behavior reflects normal dispersion in the transparency region and follows the Kramers–Kronig relation between real and imaginary parts of the dielectric function. Around 5–6 eV, where the extinction coefficient $k(E)$ reaches its maximum, the refractive indices exhibit a decrease with increasing photon energy, a hallmark of anomalous dispersion. This interplay confirms the correlation between absorption maxima and refractive index anomalies. The anisotropy in n (about 0.5 between $n_{||}$ and $n_{\perp}$) is relatively strong and arises from the layered crystal structure of Cu_4SeTe , where electronic transitions differ between in-plane and out-of-plane polarizations. The estimated numerical uncertainty of the refractive index and extinction coefficient values does not exceed 0.1 due to the chosen k -point mesh density.

Fig. 6 illustrates the reflection coefficients of Cu_4SeTe for both polarizations. The spectra display moderate reflectivity in the low-energy region, followed by enhanced reflection in the 3–5 eV range, in agreement with the strong absorption onset. Such reflectivity behavior is comparable to that of other layered chalcogenides and highlights the polarization dependence of the optical response.

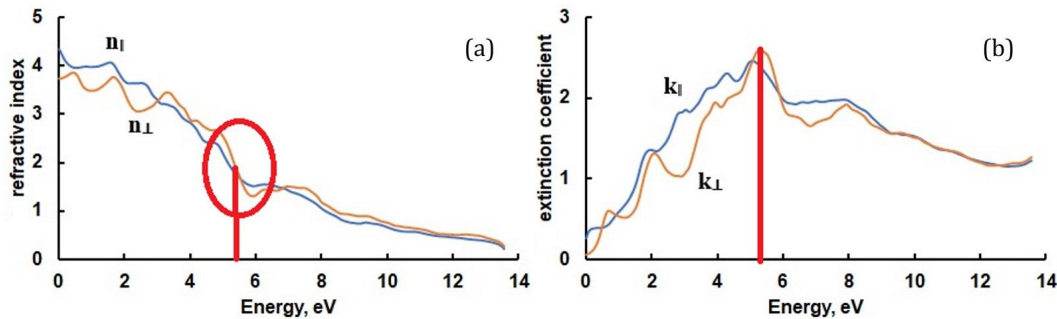


Fig. 5. The dependencies of refractive indices (a) and extinction coefficients (b) for in-plane and out-of-plane polarizations. A pronounced anisotropy (~ 0.5 between $n_{||}$ and $n_{\perp}$) is observed. n shows normal dispersion in the transparency region and abnormal dispersion near the 5–6 eV absorption maxima. Numerical uncertainty: $\Delta n, \Delta k \lesssim 0.1$. The red line (panel (b)) corresponds to the range in which the extinction coefficient $k(E)$ reaches its maximum, while the red circle (panel (a)) – to the range where the refractive indices exhibit the anomalous dispersion.

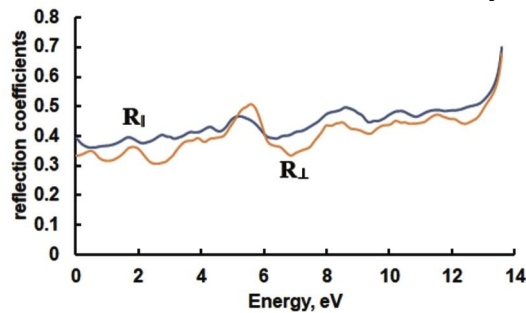


Fig. 6. Reflection coefficients of Cu_4SeTe for various polarizations of incident light.

The absorption coefficient spectra are shown in Fig. 7, with the Y-axis units corrected to cm^{-1} . The calculated $\alpha(E)$ reaches values of $\sim 10^5 \text{cm}^{-1}$ in the 2–4 eV range, which is now explicitly visible in the revised plot. This absorption level is comparable to or exceeds that of benchmark photovoltaic and photodetector materials such as CdTe and Cu(In,Ga)Se_2 . A coefficient of this magnitude implies that nearly complete light harvesting can be achieved in films thinner than 1 micrometer, making Cu_4SeTe particularly well-suited for thin-film device architectures. The high absorption coefficient, therefore, confirms that Cu_4SeTe can act as an efficient absorber in optoelectronic applications requiring compact and lightweight active layers.

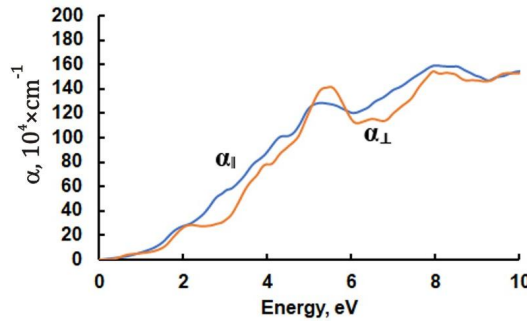


Fig. 7. Spectral dependence of the absorption coefficient $\alpha(E)$ for Cu_4SeTe under different polarizations of incident light.

Fig. 8 displays the spectral dependence of the real and imaginary parts of the complex optical conductivity. The pronounced peak in the real part of the optical conductivity, $\sigma(E)$, within the 2.5–5 eV energy range supports a strong electronic response in the visible spectrum. As depicted in Fig. 2 and 3, this energy region corresponds directly to the maximum in the density of states, which confirms the origin of this peak. The inclusion of dispersion of the imaginary part of conductivity further highlights the role of bound-bound electronic transitions and confirms the strong dispersive behavior in this energy region. The simultaneous analysis of real and imaginary parts of conductivity reveals a consistent picture in which strong interband excitations dominate the visible-to-UV spectral response.

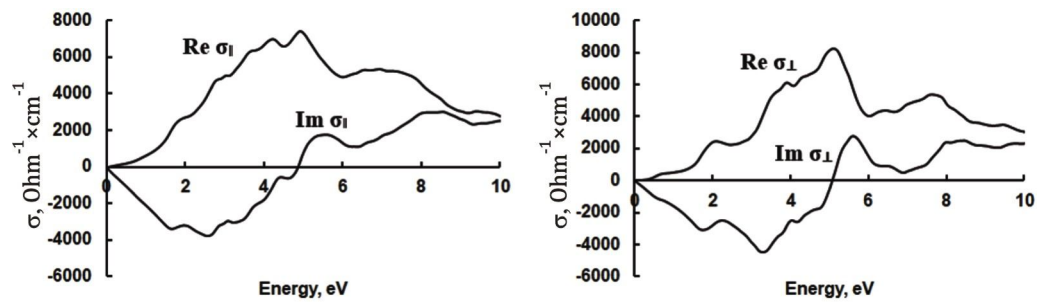


Fig. 8. Spectral dependence of the real and imaginary parts of the complex optical conductivity of Cu_4SeTe under different polarizations of incident light.

Taken together, these optical properties establish a direct connection between the electronic structure and the macroscopic optical response of Cu_4SeTe . The agreement between $\varepsilon(E)$, $n(E)$, $k(E)$, $\alpha(E)$, $\sigma(E)$, and the calculated PDOS underscores the robustness of the results and the predictive power of the first-principles approach. Importantly, the combination of high absorption, significant optical anisotropy, and correlated interband transitions positions Cu_4SeTe as a multifunctional material. Its high absorption coefficient supports thin-film photovoltaic applications, while the polarization dependence of n and k suggests potential in polarization-resolved photodetectors, optical filters, and waveguide-integrated sensors. In addition, the broadband response and semimetallic character make Cu_4SeTe a promising candidate for thermophotovoltaic converters and other energy-harvesting technologies.

To contextualize the physical properties of Cu_4SeTe , Table 1 offers a comparative overview of the structural, electrical, and optical parameters of Cu_2Se , Cu_2Te , and Cu_4SeTe . The comparison emphasizes the intermediate nature of Cu_4SeTe regarding conductivity and Seebeck coefficient. Notably, the available data indicate that Cu_4SeTe could serve as a promising multifunctional material bridging binary copper chalcogenides.

Table 1. Comparative structural and electrical properties of Cu₂Se, Cu₂Te, and Cu₄SeTe

Parameter	Cu ₂ Se	Cu ₂ Te	Cu ₄ SeTe
Space group	Fm $\bar{3}$ m (cubic) [7]	Pnma / P $\bar{3}$ m1 (orthorhombic / trigonal) [8]	R $\bar{3}$ m (trigonal) [12]
Measurement temperature range, K	300–800 [7,13]	300–700 [8]	80–320 [12]
Electrical conductivity, S/cm	~500–2000 [7,13]	~300–1000 [8]	~720 at 300 K (this work)
Hole mobility, cm ² /V·s	~30–40 [7]	~15–25 [8]	~20 (this work)
Seebeck coefficient, μ V/K	~180–220 [7,13]	~150–200 [8]	~170 (this work)
Conductivity type	p-type [7,8]	p-type [8]	p-type (this work)
Absorption coefficient α , cm ⁻¹	10 ⁵ –10 ⁶ (visible range) [9]	10 ⁴ –10 ⁵ [9]	~10 ⁵ (2–4 eV range, this work)

Overall, Cu₄SeTe combines the features of Cu₂Se and Cu₂Te while providing added tunability through its mixed-anion composition. Its distinctive blend of semimetallic behavior, strong optical transitions, and structural anisotropy emphasizes its potential as a next-generation optoelectronic material worthy of further theoretical and experimental investigation.

3. Conclusions

In this work, the electronic structure and optical properties of the ternary compound Cu₄SeTe are systematically examined using first-principles density functional theory. The results show a semimetallic electronic character, with the valence band mainly influenced by Cu 3d and Se/Te p orbitals. Conversely, the conduction band mostly consists of Cu 4s and Se/Te p states. This orbital hybridization creates a high density of states near the Fermi level, enabling strong interband transitions.

The calculated optical spectra demonstrate strong light-matter interactions in the visible-to-near-UV range. In particular, the absorption coefficient $\alpha(E)$ reaches values around 10⁵ cm⁻¹ between 2 and 4 eV, while the optical conductivity $\sigma(E)$ shows prominent peaks in the 2.5–5 eV region. These results establish Cu₄SeTe as a strong absorber well-suited for thin-film optoelectronic devices such as solar cells, photodetectors, and thermophotovoltaic converters. The observed optical anisotropy further indicates potential for polarization-sensitive applications like integrated waveguide sensors and optical filters.

Compared to the binary phases Cu₂Se and Cu₂Te, the ternary Cu₄SeTe phase combines beneficial features of both, connecting their functionalities while adding more tunability through its mixed-anion composition. This combination of semimetallic transport, high absorption efficiency, and anisotropic optical response makes Cu₄SeTe a promising multifunctional material for future energy conversion and optoelectronic applications.

Future research should focus on the role of dopants, intrinsic defects, and nanostructuring in controlling the electronic and thermal transport properties of Cu₄SeTe. Additionally, experimental investigations of its optical response, carrier dynamics, and thermal conductivity are essential for validating the theoretical predictions and fully evaluating the material's potential in advanced device applications.

Conflict of Interests. The authors declare that they have no conflicts of interest, whether financial or personal, that could have influenced the work reported in this paper.

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Анотація. У цій роботі ми представляємо комплексне теоретичне дослідження електронної структури та оптичних властивостей кристалів Cu₄SeTe з використанням розрахунків за допомогою теорії функціоналу густини (DFT), з перших принципів. Аналіз охоплює зонну структуру, повну та часткову густину станів (DOS та PDOS), комплексну діелектричну функцію, показник заломлення, коефіцієнт екстинкції, відбивну здатність, коефіцієнт поглинання та оптичну провідність. Результати показують, що Cu₄SeTe поводить себе як напівметал з гібридизованими станами Cu 3d та Se/Te p, що домінують у валентній області, тоді як стани Cu 4s та Se/Te p формують зони провідності. Розраховані оптичні спектри демонструють сильне поглинання у видимому діапазоні (2–4 eV), з коефіцієнтами поглинання, що досягають приблизно 10⁵ см⁻¹, разом із помітними міжзонними переходами та суттєвою оптичною анізотропією. Ці результати свідчать про те, що Cu₄SeTe є перспективним багатофункціональним матеріалом з потенційним застосуванням у тонкоплівкових фотоелектричних елементах, фотодетекторах та термоелектричних пристроях.

Ключові слова: Cu₄SeTe, *ab initio* розрахунки, оптичні властивості, густина станів, діелектрична функція, коефіцієнт поглинання, відбивна здатність