

**AN AB INITIO INVESTIGATION OF COPPER SULFANITES:
BULK AND LAYERED NANO STRUCTURE**

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY**

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**AN AB INITIO INVESTIGATION OF COPPER SULFANITES: BULK
AND LAYERED NANO STRUCTURE**

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Certificate

This is to certify that the thesis entitled ‘An *ab initio* investigation of copper sulvanites: Bulk and layered nano structure’ submitted by Shri Bernard Lalroliana, for the degree of Doctor of Philosophy of the Mizoram University, Aizawl, embodies the record of original investigations carried out by him under my supervision. The thesis presented is worthy of being considered for the award of the Ph. D. degree. This work has not been submitted for any degree to any other University/Institute.

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DECLARATION
MIZORAM UNIVERSITY
AUGUST, 2025

I Bernard Lalroliana, hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to do the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University/Institute.

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This Thesis is Dedicated
to
My Parents
Joseph Lianzama (1949-2002)
&
Maria Tingthianhoih (1961-1999)

CHAPTER 1
INTRODUCTION

1

Introduction

This section discussed introduction on the history, general properties integrated with literature review of Copper Sulvanite compounds (CSCs) in subsection 1.1, followed by the conceptual discussion/explanation to photovoltaic (PV) and thermoelectric (TE) properties in subsection 1.2 and 1.3 respectively, concluded by thin film/surface slabs discussion in subsection 1.4.

1.1 Copper Sulvanite Compounds

Sulvanites are those compounds consisting sulfides of Copper and Vanadium. The first such compound to be described is Copper tetrathiovanadate or copper vanadium sulphate, which naturally occurs in hydrothermal copper deposits containing vanadium as primary sulfide and has the chemical formula Cu_3VS_4 . From a review article by Prado-Rivera *et al* (Prado-Rivera et al., 2021) we have a broad and general idea on the present studies, previous findings, and the promising property of sulvanites as the next generation energy materials. Pauling and Hultgren (Pauling & Hultgren, 1933) were perhaps the prominent pioneers in scientific approach to defining the crystal structure of Cu_3VS_4 in the year 1933 using oscillation and Laue photography. The compound Cu_3VS_4 crystallizes in a simple cubic structure, belonging to the P-43m space group, with a lattice constant of 5.375 Å. Following this, the generic formula for copper sulvanite Cu_3MX_4 is obtained where M can take transition metal V, Nb, and Ta while X are chalcogen atoms S, Se, and Te (G. Delgado et al., 2009; G. E. Delgado et al., 2007; Hulliger, 1961; Klepp & Gurtner, 2000; Lu & Ibers, 1993; Trojer & Materials, 1966; Van Arkel & Crevecoeur, 1963) as shown in Figure 1.1.

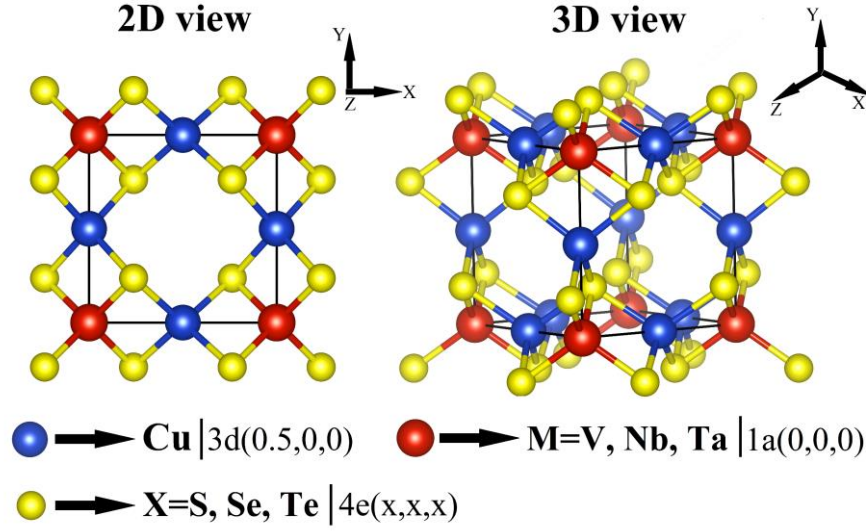


Figure 1.2. Bulk crystal structure of Cu_3MX_4 with Wyckoff's position of the respective atoms.

The only notable doping investigations on copper sylvanite compounds were conducted by Chen *et al.*, (Chen et al., 2017), who synthesized various compositions of $\text{Cu}_3\text{NbS}_{4-x}\text{Se}_x$, and S. Ikeda *et al.*, (Ikeda et al., 2019), who explored chemical substitution in $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ for photocatalytic and photoelectrochemical H_2 evolution. Chen's study found that the doped structure still resembles the parent Cu_3VS_4 cubic crystal, with an increased lattice parameter, successfully tuning the optical band gaps (E_{opt}) from 2.6 to 2.2 eV while enhancing optical absorption and thermoelectric performance. In the experimental aspects of thin films, Lv *et al.*, (Lv et al., 2012) successfully prepared nano- Cu_3VS_4 thin film of thickness 220 nm by pulsed laser deposition (PLD) method. Using spectroscopic ellipsometry, the optical band gap is found to be 1.35 eV. Subsequently, Syu *et al.*, (Syu et al., 2022) developed a solar cell based on these thin films with 3.11% efficiency. Liu *et al.*, (M. Liu et al., 2020) have also reported Cu_3VSe_4 nanosheets having thickness of 604 nm with 1.8 eV optical band gap. Further, Newhouse *et al.*, (Newhouse et al., 2009) have designed Cu_3TaS_4 and Cu_3TaSe_4 thin films of 200 nm thickness having band gap of 2.70 and 2.35 eV respectively, using the two-step growth technique involving PLD and *ex-situ* annealing. In all reported studies, copper sylvanite compounds have been observed to exhibit a preferential growth orientation along the (100) crystallographic plane.

Furthermore, to our knowledge, no theoretical investigations on the thin-film properties of these compounds have been conducted.

The availability and ease of access to energy have been one of the driving factors of development for mankind. The rapid growth in population, along with the extensive use of machinery, has led to further supplementary energy demands. It is anticipated that population growth is expected to increase continuously, thus, energy demands are also projected to rise in folds. This upsurge in energy demands has ultimately led to the growth of energy production as well as consumption; which is met chiefly from non-renewable energy sources, commonly fossil fuels. Nevertheless, while fossil fuels continue to play key importance in the energy sector, they are inherently finite and susceptible to depletion. Moreover, their utilization has a detrimental environmental impact due to the release of toxic by-products and pollutants. So, for the present as well as future generations, it is imperative to explore novel energy sources and energy harvesting means that satisfy the growing demands while simultaneously eliminating or minimizing the adverse effects. This impact led researchers to approach green energy that might be met through renewable sources.

Solar energy is world-wide acknowledged for its sustainability and environmental friendliness, as it is both a renewable and green energy source. Owing to the extensive depletion of fossil fuel reserves, solar photovoltaic technology, which effectively harnesses solar energy for conversion into electrical power, has emerged as a prominent and sustainable energy alternative, has garnered scientific attention over several decades back. Photovoltaic devices based on silicon technology have more or less attained their full potential, which have been industrially manufactured and widely used all over the world. However, it has certain limitations with regards to high cost of manufacturing in silicon based photovoltaic cells. Over the past decades, alternative technologies to silicon-based photovoltaics have been extensively investigated. However, the majority of these emerging technologies remain at the laboratory research stage and have yet to achieve large-scale industrial production. Among the emerging photovoltaic technologies, those utilizing copper indium gallium diselenide $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{S}_2$ (CIGS) (Ramanujam & Singh, 2017) and cadmium telluride

(CdTe) (Bai et al., 2011) as absorber materials have demonstrated highly promising results in terms of efficiency and scalability. However, these materials present certain limitations, primarily the high cost of indium and tellurium, and the toxicity associated with cadmium, which poses environmental and safety concerns. So, a more convenient, cheaper and more eco-friendly materials will be highly suitable due to the afore mentioned issues. With this understanding, more attention is given to alternative PV absorbers that will be Earth-abundant, sustainable, and non-toxic. In this regards, sulvanite compounds might provide a promising solution and are now being investigated as a material for photovoltaic devices.

The potential of copper sulvanite compounds (CSCs) for applications in both PV and TE materials has been extensively investigated. Especially in theory, distinct literature reports that these groups of compounds exhibit promising properties since their band gaps lie close to the optimum value of ~ 1.5 eV for PVs. At ambient pressure, Kehoe *et al.*, (Kehoe et al., 2015, 2016) extensively explored the same within the GGA formalism and hybrid functionals and effective Hubbard correction (U) of 5.2 eV in Cu-d orbitals. For Nb-based compounds, the authors report that implementing U correction approximates band gaps better to experimental results compared to hybrid HSE06 functional. From an analogous investigation by Espinosa-García, W.F. *et al.*, (Espinosa-García et al., 2018) authors report quite similar optical band gaps (OBG) for similar functionals in addition to peculiar trends when using the computationally presumed accurate and heavy time-dependent DFT-GW calculation. Hersh P.A. (Hersh, 2007) and Chen *et al.*, (Chen et al., 2017) independently measured the experimental OBG of Cu_3NbS_4 and Cu_3NbSe_4 as 2.56, 2.13 eV and 2.6, 2.2 eV respectively, while experimental measurements for Cu_3NbTe_4 is yet to be achieved. The potency for TE materials can be understood from the unitless efficiency merit ZT. Enhancing PF is quite a challenge to researchers since its constituent terms are coupled, and enhancement in one term tends to effectively subdue the other and vice versa. For this same reason, techniques for minimizing thermal conductivity to improve ZT have been an interesting area for researchers. CSC for potential TE materials has been reported in several literatures (Chen et al., 2017; Haque, 2021; Hong et al., 2017; X.-P. Liu et al., 2019). In theory, Nb-based CSCs are predicted to

have high $ZT > 1$ at high temperatures, suggesting high TE performance. It is also known that the enhanced ZT in these compounds ascend not only from their high PF, more over from their intrinsically low κ_l . Thus, insofar as theory is concerned, CSC exhibits promising properties for potential light absorbers as well as good TE materials.

1.2 Photovoltaics

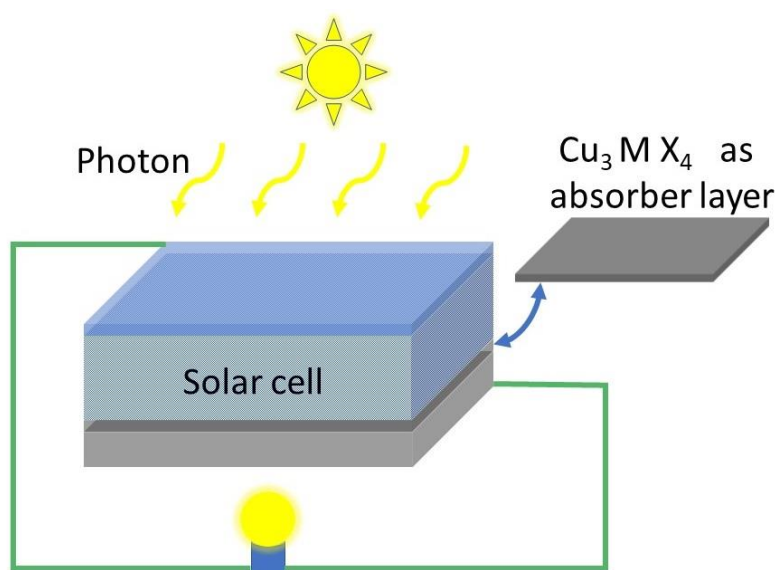


Figure 1.3. Graphical illustration on the working principle of a solar cell with certain layers, emphasizing the absorber layer.

Figure 1.3 illustrates the basic working principle of solar cells consisting of several layers where sunlight is directly absorbed to generate electric current. Photovoltaic devices, commonly raised to as solar cells, are systems that convert solar energy directly into electrical current via the photovoltaic effect. The sun is a great source of energy with solar constant of $1.366 \times 10^3 \text{ Wm}^{-2}$ reaching the earth's surface yearly, making it the most abundant energy (Gueymard, 2004). Maximum intensity of light reaching the surface arrives from the spectrum within the visible region, which tally to wavelengths $\sim 380 \text{ nm} - 780 \text{ nm}$ ($\sim 3.2 \text{ eV} - 1.6 \text{ eV}$), i.e., from UV to red. Therefore, harnessing this portion of the solar spectrum is particularly advantageous

for energy generation due to its higher photon flux. Semiconductors with appropriately tuned band gaps can absorb these photons effectively, facilitating the excitation of electrons from the valence to conduction bands, thereby generating electrical energy. This is brought about by the absorption of certain incident photons from sunlight of specific wavelength (energy) characterised by the electronic energy gap of semiconductor. Photon with lower energy will not be absorbed and simply pass through the semiconductor, or in other words, excluded for electric current generation. The larger energy photons (photon energy higher than the band gap) will still get absorbed, with some part of the energy utilized for interband transition while the excess energy will get dissipated as heat, warming up the semiconductor device. This suggests that an optimal photovoltaic device should possess a band gap closely aligned with the energy range of visible light, enabling efficient absorption and conversion of solar energy. Semiconductors with high band gaps would possess low photovoltaic efficiency by rejecting lower photon energies; while a narrow band gap semiconductor would absorb majority of incident light, heating up the device with the excess energy, hindering photovoltaic performance and impairing device durability. Solar cells generally consist of several layers ranging from 4-7 depending upon the purpose, material utilized, and type of solar cells, etc. Among such layers, the absorber layer plays a pivotal role in photovoltaic devices, as it is the region where incident light is absorbed, leading to the initiation of electron-hole pairs that contribute to the electric current. This current study will primarily focus on copper sylvanite compounds, evaluating their potential as high-performance materials for solar energy absorption. Generated electron-hole pair are then collected in separate terminals to produce electric current. The generated electron-hole pair however, could recombine within this same region hindering the efficiency and generation of electric current. To minimise such phenomenon of recombination of holes and electrons, the absorber layer should be thin enough so as to lower the probability of recombination rates. For this, the absorption coefficient, which primarily measures how readily light is absorbed in a medium, must be sufficiently high in the visible spectrum of light for the thin absorber layer. This is because for low absorption coefficient absorbers, majority of readily absorbable photons from sunlight are transmitted through the material without

generation of electron-hole pair. For such low absorption coefficient absorber layers, the layer must be comparatively thicker which will hinder photovoltaic performance due to higher probability recombination rates. It is well understood that an efficient and effective photovoltaic absorber should exhibit an optimal band gap closely matching the energy range of visible light, along with a high optical absorption coefficient to enable sufficient light absorption even at reduced material thicknesses, thereby supporting the development of thinner and more cost-effective devices.

1.3 Thermoelectrics

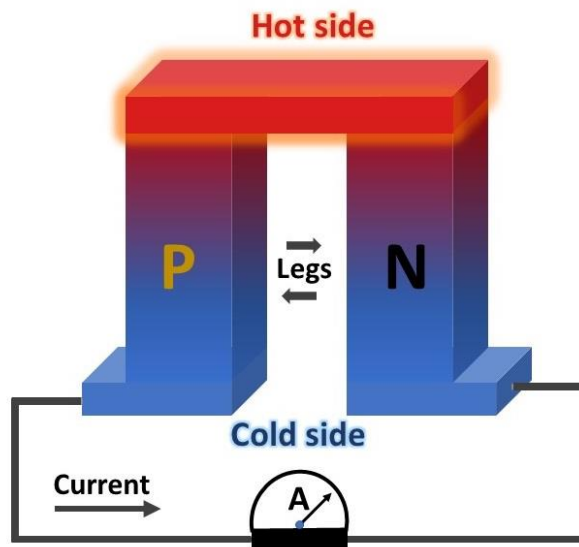


Figure 1.4. Illustration on working of a simple Thermoelectric device demonstrating electric current generation due to temperature gradient across two ends of P-type and N-type semiconductor.

When energy is utilized for useful work, a certain part of the energy is always dissipated to the surroundings or converted into heat. Further, heat generation also arises through imperfect energy conversion means, friction from mechanical as well as electronic devices, combustion, etc. Globally, useful work done by heat is estimated to be only 20%, implying an astonishing 80% of the total heat energy being lost to the environment, which could directly contribute to global warming (Bian, 2020). Given the amount of heat loss directly to the environment, it is apparent that harnessing this

unused energy could assist in global energy demands while simultaneously minimizing the global warming effect. Apart from numerous heat energy harvesters, this study puts its interests on the theoretical investigations of electricity generation prospects from heat energy, through thermoelectric devices. Thermoelectric system harness waste heat and convert it into usable electricity without the requirement of any mechanical moving parts. In its simplest sense, thermoelectric device based its principle on the phenomenon that when a solid (semiconductor) is heated on one side, charge carriers diffuse into the relatively colder side, generating an induced potential. This induced potential can then be exploited for generating electric current for various utilization purposes. A fundamental thermoelectric device comprises p-type and n-type semiconductor legs connected in series via a metallic (electrically conductive) contact, with the legs aligned in a parallel configuration, as presented in Figure 1.4. When heat is absorbed (source) or applied to ends of the two legs, charge carriers diffuse towards the cold side (sink) and into the opposite leg through the metal contact to generate electric current. This process continues as long as certain temperature difference is maintained. Ideally, charge carriers exhibiting high transport efficiency are preferred as this will enhance the thermoelectric current generation meanwhile could reduce efficiency by increasing the sink temperature due to higher diffusion rates towards the sink. For this reason, the source and sink should respectively absorb and reject heat rapidly to maintain the temperature difference. Materials with high electrical but low thermal conductivity are ideal for thermoelectric devices. However, low-melting, brittle materials are unsuitable due to operating temperature constraints. Given current theoretical and computational limitations, this study explores copper sylvanite compounds for a single semiconductor leg.

1.4 Thin film/Surface slabs

Thin films, in materials science context, possess thickness in the order of 1 μ m or less, often still exhibiting similar properties to their bulk counterpart. Thin films, however should not be confused to 2D materials, which essentially exist in a single plane, comprising of few atomic or some even to single atomic layers. This so-called slab surfaces or thin films that is scaled down from bulk structures, have advanced

today's technology and devices in numerous ways, characterized by their thickness, geometry, and structure (Acosta, 2021). In advance electronic devices like MOSFETs, SiO₂ thin films acts as insulator for ease of fabrication due to their exceptional properties (Rao & Shekhawat, 2013). The emergence of thin film photovoltaic devices like CIGS and CdTe-based materials revolutionized the solar cell industry, attaining an astonishing 23.3% and 22.1% efficiency respectively; an additional advantage being low production costs due to feasible thinner absorber layer owing to higher absorption coefficient (Sundaram et al., 2018). Also, due to the unique properties of thin films, state-of-the-art flexible photovoltaics can be engineered on a flexible substrate, broadening the scope of application (Khrypunov et al., 2006). Other applications include coating materials/devices for structural enhancement by preventing wear and tear, thereby elongating the material's lifespan (Choy, 2003); providing biocompatible and functional properties like tissue engineering substrate, antimicrobial coating, invasive devices, and drug delivery, etc (Piedade et al., 2018). Although many applications remain undefined, the impact of thin film in today's modern world can be realized. Following this notion, we stressed this work on the DFT thin film investigation of copper sulvanites. Perhaps the physical world's close resemblance to thin films can be approached in theory through DFT by truncating their bulk structures in specific directions, resulting in so-called surface slabs. In DFT, the unit structures are always treated to repeat infinitely in all directions. Bulk structures are truncated in specific Miller index plane like (100), (111), (110), etc., dividing the then bulk structures into two new sets of slabs. The two slabs are then separated with certain thickness by introducing vacuum of desirable thickness such that there exists negligible or virtually zero interaction between them while still maintaining infinite repetition along the axis parallel to the divider Miller index planes. The infinitely repeated sets of these non-interacting slabs constitute DFT surface slabs, and for the same, all calculated properties will arise due a single surface slab only. The visualization of this approach for generating surface slabs is shown in Figure 1.5.

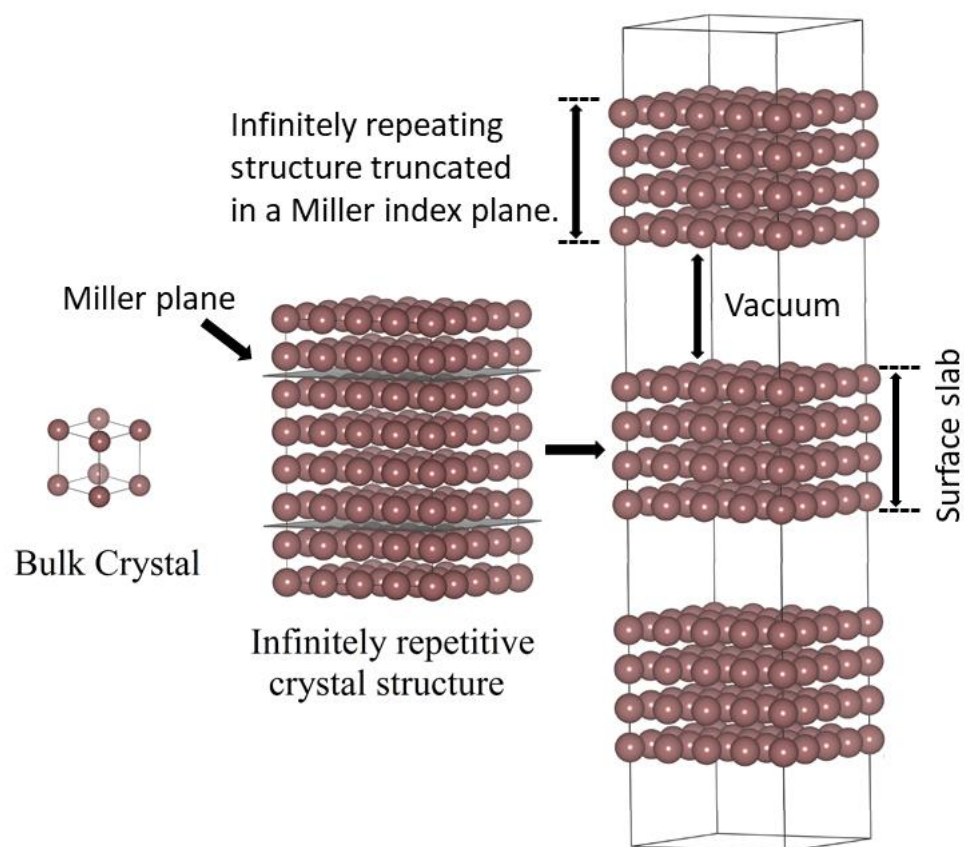


Figure 1.5. Detailed illustration of DFT surface slab with certain atomic layer thickness modeled from infinitely repeating bulk crystal structure.

In contrast to bulk calculations, surface slab enables the explicit representation of a material's properties, facilitating in-depth examination of characteristics unique to that surface, such as surface energy, adsorption behaviours, surface reconstructions, surface-based devices, surface metallicity and half-metallicity, etc.

CHAPTER 2
THEORETICAL FORMALISM
AND
METHODOLOGY

2

Theoretical Formalism and Methodology

Theoretical approach to *ab initio* calculations will be performed using DFT. Instead of the complex many-body wave function formalism reliant on all electron coordinates, DFT simplifies many-body problems by expressing ground-state properties as functionals of the single-particle electron density. The collection of non-interacting systems that effect the external field and unambiguously describe the behaviour of the solids crystalline systems.

2.1 The Many-Body Hamiltonian

From quantum mechanics, the only exact solutions to the Schrödinger's wave equation exist perhaps only for the simplest element, Hydrogen, which consists of a single proton and electron. For N electron system, the solution of the many-electron Schrödinger equation becomes a complicated 3N variable. This problem further escalates when dealing with realistic approach to materials, where atoms virtually become innumerable, each containing several electrons, making it practically impossible to solve, even with approximations.

The Hamiltonian of Schrödinger's wave equation can be expressed as

$$\hat{H}\Psi=E\Psi \quad (2.1)$$

where $\hat{H}$ is Hamiltonian and E is the eigenvalue for the quantum mechanical state Ψ . Further, the $\hat{H}$ of m nuclei with n number of electrons under the influence of electron-nucleus interaction can be written as (in atomic units)

$$\hat{H}=-\frac{1}{2}\sum_{j=1}^m\frac{\nabla_{r_j}^2}{m_j}-\frac{1}{2}\sum_{i=1}^n\nabla_{r_i}^2-\sum_{i=1}^n\sum_{j=1}^m\frac{Z_j}{|R_j-r_i|}+\sum_{i=1}^n\sum_{j>i}^n\frac{1}{|r_j-r_i|}+\sum_{i=1}^m\sum_{j>i}^m\frac{Z_jZ_i}{|R_j-R_i|}$$

(2.2)

where m_j is mass of the nucleus at R_j , r_i is the position vector of the i^{th} electron, $\nabla_{R_i}^2$ and $\nabla_{r_i}^2$ being the Laplacian operators. The nuclei and electron kinetic energy is represented by the first two terms while the e-n and n-n interaction being represented in the third term of the Equation 2.2.

The Born-Oppenheimer (Born & Oppenheimer, 1927) approximation treats the nucleus as static particles due to its immense mass difference to electrons, consequently resulting in constant Coulomb interaction. The nuclei's kinetic energy thus could be neglected from the total Hamiltonian. Equation 2.3 provides a simplified relation of the multi-electron Hamiltonian when the nuclear-nuclear interaction is treated classically.

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^n \nabla_{r_i}^2 - \sum_{i=1}^n \sum_{j=1}^m \frac{Z_j}{|R_j - r_i|} + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{|r_j - r_i|} \quad (2.3)$$

2.2 Hartree-Fock Theory

The challenge of solving the 3N-dimensional Schrödinger equation has been previously discussed. However, this complexity can be significantly reduced to just three degrees of freedom by approximating the system as non-interacting electrons, a method known as the Hartree-Fock (HF) approximation (Echenique & Alonso, 2007). The final Schrödinger equation for N-single electron using HF method is expressed as

$$\left[-\frac{1}{2} \nabla_{r_i}^2 - \sum_{j=1}^M \frac{Z_j}{|R_j - r_i|} + V_{\text{HF}}(r_i) \right] \Phi_i(r) = E_i \Phi_i \quad (2.4)$$

where V_{HF} is the effective HF potential and represents average electrostatic potential on the i^{th} electron due to all other electrons in the system.

$$V_{\text{HF}}(r_i) = \sum_j (J_j(r_i) - K_j(r_i)) \quad (2.5)$$

here, $\mathcal{J}$ and $\mathcal{K}$ represents the Coulomb operator potential of the electron at r_1 and the exchange contribution to V_{HF} respectively.

Hartree-Fock theory provides an approximated solution to the many-body Schrödinger equation, where the total wavefunction (Φ) can be given by a single Slater determinant of Spin-Orbitals (Φ_i). Due to Coulomb repulsion among the electrons, the position of each electron varies independently. The Hartree-Fock method neglects Coulomb interactions, yielding an approximate ground-state energy (Tew et al., 2007). To improve accuracy, density functional theory (DFT) incorporates both exchange and correlation potentials.

2.3 Density Functional Theory

Density Functional Theory (DFT) is a quantum computational method that models electron systems using density functionals instead of individual interactions. By expressing the ground-state functional in terms of single-particle electron density, DFT simplifies many-body problems compared to wave function formalism, which depends on all electron coordinates. Its foundation is based on two theorems by P. Hohenberg and W. Kohn (Hohenberg & Kohn, 1964).

Theorem 1: For any system of interacting electrons in an external potential $V_{\text{ext}}(\mathbf{r})$, the potential is determined uniquely, except for a constant, by the ground state particle density $\rho(\mathbf{r})$.

Theorem 2: A universal functional for the energy $E(\rho)$ in terms of density $\rho(\mathbf{r})$ can be defined, valid for any external potential $V_{\text{ext}}(\mathbf{r})$. For any particular $V_{\text{ext}}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of this functional and the density $\rho(\mathbf{r})$ that minimizes the functional is the exact ground state density $\rho_0(\mathbf{r})$.

The queries is reduced to the Schrodinger-like equation following additional modification by Kohn and Sham (KS) (Kohn & Sham, 1965), involves introducing an

auxiliary non-interacting electron system, where electrons experience an effective external potential $V_{\text{eff}}(\mathbf{r})$, governed by the variational principle:

$$(\hat{H}_{\text{KS}} - \epsilon_i)\phi_i(\mathbf{r}) = 0 \quad (2.6)$$

where ϵ_i are the eigenvalues and $\hat{H}_{\text{KS}}$ is the effective Hamiltonian given by

$$\hat{H}_{\text{KS}} = -\frac{1}{2}\nabla^2 + V_{\text{eff}} \text{ (Hartree units)} \quad (2.7)$$

further

$$V_{\text{eff}} = V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \quad (2.8)$$

The second term is Hartree potential

$$V_{\text{Hartree}} = e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.9)$$

and the third term is exchange-correlation potential defined as,

$$V_{\text{xc}} = \frac{\delta E_{\text{xc}}(\rho)}{\delta \rho(\mathbf{r})} \quad (2.10)$$

Here, E_{xc} represents the disparity between the kinetic and internal interaction energies of the true interacting many-body system and those of the auxiliary single-particle system, where electron-electron interactions are exchanged by the Hartree energy. The electron density is determined from single-electron orbitals.

$$\rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2 \quad (2.11)$$

and the overall electron count is

$$N = \int \rho(\mathbf{r}) d\mathbf{r} \quad (2.12)$$

Within the Kohn-Sham (Noel et al.) approach, the expression for the ground state energy functional turns out to be

$$E[\rho]=T_s[\rho]+\int V_{\text{ext}}(r)\rho(r)dr+E_{\text{Hartree}}[\rho]+E_{\text{xc}}[\rho] \quad (2.13)$$

The single particle kinetic energy T_s is given by

$$T_s[\rho]=\sum_{i=1}^N \int \phi_i^*(r)(-\frac{\hbar^2}{2m}\nabla^2)\phi_i \quad (2.14)$$

These equations have single particle form with the potential that must be found self-consistent with the resulting density. The above formulae represent the KS scheme for electrons in a solid of non-spin polarized state.

To investigate half-metallic properties, the spin-density functional formalism is employed by introducing two spin densities, $\rho^\uparrow(r)$ and $\rho^\downarrow(r)$. Except for the exchange-correlation term, these densities satisfy the Kohn-Sham (KS) equations under the same effective potential as previously described. The spin-dependent exchange-correlation potential can now be expressed as:

$$V_{\text{xc}}^{\text{cr}}[\rho^\uparrow, \rho^\downarrow; r] = \frac{\delta E_{\text{xc}}(\rho^\uparrow, \rho^\downarrow)}{\delta \rho(r)} \quad (2.15)$$

Approximations are required to solve Equation 2.6, as the exact exchange-correlation term is only known for a homogeneous electron gas. The most widely used are the Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA). In LDA, the exchange-correlation energy density per electron is assumed to match that of a homogeneous electron gas (Kohn & Sham, 1965).

$$E_{\text{xc}}^{\text{LDA}}[\rho] = \int \epsilon_{\text{xc}}(\rho(r))\rho(r)d^3r \quad (2.16)$$

where $\epsilon_{\text{xc}}^{\text{hom}}$ is the addition of the exchange and correlation energies of the homogenous electron gas of density $\rho(r)$. In addition to the electron density, GGA (Wang & Perdew, 1991) includes its local gradient into the exchange-correlation functional.

$$E_{xc}^{GGA}[\rho] = \int \varepsilon_{xc}(\rho(r), \nabla\rho(r))\rho(r)d^3r \quad (2.17)$$

For the basis sets to express the KS orbitals, there are three core strategies practiced nowadays, namely, the Pseudopotential methods, the Full Potential methods, and the Green's function-based methods.

2.4 PAW Pseudopotential

The complex many-electron Schrödinger equation can be greatly simplified by categorizing the electrons into two main groups: valence electrons and inner (nucleus-bound) electrons. The electrons located closer to the nucleus are tightly bound and have limited involvement in chemical bonding. These inner electrons also provide partial shielding for the nuclear charge, effectively forming a semi-rigid structure referred to as the "core." In contrast, valence electrons, which reside in the outer orbitals, are chiefly accountable for the bonding behavior of atoms, particularly in materials like metals and semiconductors. This distinction allows for the approximation that core electrons can be neglected in many computational models, simplifying the atom to an ionic core that interacts only with its valence electrons. To model this interaction efficiently, the pseudopotential approach is employed, with the Projector Augmented Wave (PAW) method (Blöchl, 1994) being foremostly accurate and widely used techniques. In this framework, the Kohn-Sham (KS) equations are solved exclusively for the valence electrons, while pseudopotentials are carefully constructed to reproduce the correct scattering behavior outside a defined core radius. This suggestively lessens the computational burden, as pseudopotentials need to be calculated only once per atom type. Besides, relativistic effects are encompassed in the core pseudopotentials but can be omitted from valence-state calculations, and the method removes the singularity of the ionic potential at atomic lattice sites.

2.5 DFT + U

The U correction accounts for the strong on-site Coulomb interaction of localized electrons using a Hubbard-like term. The Hubbard Hamiltonian primarily describes strongly correlated states in d and f orbitals, while other valence electrons follow standard DFT approximations. As the number of d and f electrons increases, Coulombic repulsion intensifies, generally requiring a larger U correction. This correction, known as the Hubbard potential (U), is typically incorporated as DFT+U (Dudarev et al., 1998; Liechtenstein et al., 1995). The following formalism is based on a spin-polarized system. The approximate energy in DFT+U is expressed as the sum of the DFT-derived approximate energy and the Hubbard term contribution.

$$E_{\text{DFT+U}} = E_{\text{DFT}} + E_{\text{U}} \quad (2.18)$$

E_{DFT} represent approximated energy from DFT and E_{U} can be expressed as:

$$E_{\text{U}} = \frac{1}{2} \sum_{I\sigma B_1 B_2} U^I (\delta_{B_1 B_2} - n_{B_1 B_2}^{I\sigma}) n_{B_1 B_2}^{I\sigma} \quad (2.19)$$

where I the atomic site index, B_1 and B_2 are the magnetic quantum numbers accompanying by a specific angular momentum and U^I is the effective on-site Hubbard parameters. In the Hubbard manifold scheme, the atomic occupation matrices $n_{B_1 B_2}^{I\sigma}$ are based on the projection of the KS states wave function $u_{v,k}^{\sigma}(\mathbf{r})$:

$$n_{B_1 B_2}^{I\sigma} = \frac{1}{n_k} \sum_k \sum_j O_{j,k}^{\sigma} \langle u_{j,k}^{\sigma} | \hat{P}_{B_2 B_1 k}^I | u_{j,k}^{\sigma} \rangle \quad (2.20)$$

where k is the sampled points in the Brillouin zone, $O_{j,k}^{\sigma}$ the occupations of KS states j and σ indicate the band and spin notation in the KS wave function. Whereas, the projector on the Hubbard manifold;

$$\hat{P}_{B_2 B_1 k}^I = |\phi_{B_2 k}^I\rangle \langle \phi_{B_1 k}^I| \quad (2.21)$$

2.6 Spin Orbit Coupling (SOC)

The majority of calculations in DFT are based on non-relativistic quantum mechanics, in which spin only enters in the orbital occupations and fully decouples from spatial degrees of freedom. In major cases, the non-relativistic approximation holds which, however, becomes less accurate for electrons with non-zero angular momentum in heavier atoms. In heavier elements, particularly transition and lanthanides, the spin magnetic and orbital magnetic moment coupling could become quite significant, resulting distinct electronic properties. According to Soner Steiner, Sergii Khmelevskiy *et al.*, (Steiner et al., 2016) the PAW Hamiltonian reduces to

$$\hat{H}_{SO} = \sum_{ij} |p_i\rangle \langle \phi_i | H_{SO} | \phi_i \rangle \langle p_j | \quad (2.22)$$

H_{SO} for zeroth-order-regular approximation can be written as

$$H_{SO}^{\alpha\beta} = \frac{\hbar^2}{(2m_e c)^2} \frac{K(r)}{r} \frac{dV(r)}{dr} \vec{\sigma}^{\alpha\beta} \cdot \vec{L} \quad (2.23)$$

where angular momentum operator $\vec{L}$ is defined as $\vec{L} = \vec{r} \times \vec{p}$, $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ the (2x2) Pauli spin matrices, $V(r)$ the spherical part of effective all electron potential in the PAW spheres.

$$K_r = \left(1 - \frac{V(r)}{2m_e c^2}\right)^{-2} \quad (2.24)$$

Equation 2.23 can be re written as given below by implementing $\phi_i(r) = R_i(|r|)Y_{l_i m_i}(\hat{r})$

$$\hat{H}_{SO}^{\alpha\beta} = \frac{\hbar^2}{(2m_e c)^2} \sum_{ij} |\hat{p}_i\rangle R_{ij} \vec{\sigma}_{\alpha\beta} \cdot \vec{L}_{ij} \langle \hat{p}_j | \quad (2.25)$$

where

$$R_{ij} = 4\pi \int_0^{r_c} R_i(r) \frac{K(r)}{r} \frac{dV(r)}{dr} R_j(r) dr \quad (2.26)$$

and

$$\vec{L}_{ij} = \langle Y_{l_i m_i} | \vec{L} | Y_{l_j m_j} \rangle, \quad (2.27)$$

Y_{lm} being the real spherical harmonics.

Finally, action of the SOC operator on the PS orbitals is evaluated as

$$|\hat{\psi}_n^\alpha\rangle = \sum_{\alpha\beta} \hat{H}_{SO}^{\alpha\beta} |\hat{\psi}_n^\beta\rangle, \quad (2.28)$$

where α and β respectively are the spin-up and spin-down components of the two module spinor wave functions necessary to describe noncollinear magnetism.

2.7 Elastic Constant Calculations

Mechanical properties are generated according to Le Page and Y. Saxe *et al.*, (Le Page & Saxe, 2001) within the Debye model. Elastic moduli such as Bulk modulus (B), shear modulus (G), Young's modulus (Y) (all in units of Pa), Poisson's ratio (ν), and Pugh's ratio (B/G) are calculated within the formalism of Hill assumptions (Hill, 1952) along with their Debye temperature (Θ) (in Kelvin) (Anderson, 1963) and Grüneisen parameter (γ) (Barrera et al., 2005; Sanditov & Belomestnykh, 2011).

For cubic crystals, only the C_{11} , C_{12} , and C_{44} (in Pa), elastic constants are required for the prediction of various elastic properties. Elastic properties like B, G, Y, ν , and γ within Hill's assumption can be derived by prior consideration of Voigt (Voigt, 1889) (subscript V) and Reuss (Reuss, 1929) (subscript R) assumption.

$$B_V = B_R = \frac{(C_{11} + 2C_{12})}{3} \quad (2.29)$$

$$G_V = \frac{(C_{11} - C_{12} + 3C_{44})}{5}, \quad G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3C_{11} - 3C_{12}} \quad (2.30)$$

From Equation 2.29 and Equation 2.30, elastic properties within Hill's assumption can be obtained following the formula

$$B = \frac{B_V + B_R}{2}, \quad G = \frac{G_V + G_R}{2} \quad (2.31)$$

Subsequently, Y and ν can be calculated

$$Y = \frac{9BG}{3B+G}, \nu = \frac{3B-2G}{2(3B+G)} \quad (2.32)$$

The Grüneisen parameter can then be derived from ν using the formula

$$\gamma = \frac{3}{2} \left(\frac{1+\nu}{2-3\nu} \right) \quad (2.33)$$

Finally, the mean sound velocity (in m/s) can be obtained as

$$u_m = \left[\frac{1}{3} \left(\frac{2}{u_t^3} + \frac{1}{u_l^3} \right) \right]^{-\frac{1}{3}} \quad (2.34)$$

where u_t and u_l are transverse and longitudinal sound velocities respectively and ρ the density

$$u_t = \left(\frac{G}{\rho} \right)^{\frac{1}{2}} \text{ and } u_l = \left(\frac{3B+4G}{3\rho} \right)^{\frac{1}{2}} \quad (2.35)$$

The deduced mechanical properties B predicts resistance towards axial deformation while shear strain resistance can be inferred from G . Moreover, the Bulk modulus (B) also signifies resistance towards volume change. The ductility of a material can be obtained from Poisson's (ν) and Pugh's ratio (B/G). The critical limits for the two are at $\nu = 0.28$ and $B/G=1.75$. Below these limits, the materials/compounds are considered brittle. Further phonon calculations are calculated following the ab initio approach according to Parlinski, K., Z.Q. Li, and Y. Kawazoe (Parlinski et al., 1997). Negative phonon frequencies will indicate instability of crystals while positive values will indicate dynamical stability.

2.8 Optical properties

The influence of incident radiation on materials is analyzed through their optical properties, determined by computing the dimensionless complex dielectric constants. These constants yield various optical parameters, including the complex refractive index and absorption coefficient. The dielectric function, comprising the real ϵ_1 and imaginary ϵ_2 part is fundamental, as all other optical characteristics can be inferred from it. The complex dielectric function is mathematically expressed as:

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \quad (2.36)$$

The imaginary part of the dielectric function, $\epsilon_2(\omega)$, is directly derived from the occupied and unoccupied wave functions of the momentum matrix. It primarily represents indirect observables of the complex dielectric function, including absorption, dielectric loss, and energy loss.

$$\epsilon_2(\omega) = \frac{e^2}{\pi m^2 \omega^2} \sum_{nn'} \int_{\mathbf{k}} d^3k |\langle \vec{k}_n | \vec{p} | \vec{k}_{n'} \rangle|^2 [1 - f(\vec{k}_n)] \delta(E_{\vec{k}_n} - E'_{\vec{k}_{n'}} - \hbar\omega) \quad (2.37)$$

Using the well-known Kramers-Kronig transformation, one may extract the real part of the dielectric function $\epsilon_1(\omega)$, which represents the polarizability of materials with incoming radiation without absorbing energy (Martin, 1967):

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\epsilon_2(\omega') \omega' d\omega'}{\omega'^2 - \omega^2} \quad (2.38)$$

From this, supplementary optical characteristics like refractive index (η) and extinction coefficient (k) can be directly obtained as follows (Fox, 2002):

$$\eta(\omega) = \frac{1}{\sqrt{2}} [\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} + \epsilon_1(\omega)]^{1/2} \quad (2.39)$$

$$k(\omega) = \frac{1}{\sqrt{2}} [\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} - \epsilon_1(\omega)]^{1/2} \quad (2.40)$$

For further investigation into the photovoltaic absorber, it is essential to examine the absorption coefficient (α) from the extinction coefficient using the formula

$$\alpha(\omega) = \frac{4\pi k(\omega)}{\lambda} \quad (2.41)$$

2.9 Transport properties

The semiclassical Boltzmann transport theory proposes that electrons obey classical equations of motion between scattering events separated by a relaxation time while relying on the quantum-mechanical calculation of the electronic states. Within the constant relaxation time approximation (CRTA), according to BoltzTraP code, electron transport coefficients for example the Seebeck coefficient (S), that is potential difference generated when two ends of a TE material are maintained at different temperatures, electrical conductivity (σ), total thermal conductivity (κ_T), which is determined by two parts: the electronic part (κ_e) and the lattice part (κ_l), TE power factor (PF), etc., will be presented. The TE parameters can be calculated using the formulae (Madsen & Singh, 2006)

$$S_{\alpha\beta}(\mu, T) = \frac{1}{eTV\sigma_{\alpha\beta}(T, \mu)} \int \bar{\sigma}_{\alpha\beta}(\mu - \epsilon) \left[\frac{\partial f_{\mu}(T, \epsilon)}{\partial \epsilon} \right] d\epsilon \quad (2.42)$$

$$\sigma_{\alpha\beta}(\mu, T) = \int \bar{\sigma}_{\alpha\beta} \left[-\frac{\partial f_{\mu}(T, \epsilon)}{\partial \epsilon} \right] d\epsilon \quad (2.43)$$

$$\kappa_{e(\sigma\beta)}(\mu, T) = \frac{1}{e^2TV} \int \bar{\sigma}_{\alpha\beta}(\epsilon)(\mu - \epsilon)^2 \left[-\frac{\partial f_{\mu}(T, \epsilon)}{\partial \epsilon} \right] d\epsilon \quad (2.44)$$

α, β being the Cartesian indices, μ the chemical potential, ϵ and V the energy and volume of primitive cell respectively.

Equation 2.42 and Equation 2.43 can then be combined to calculate the PF, which has the relation

$$PF = S^2\sigma \quad (2.45)$$

A different approach is, however, implemented for calculating κ_l utilizing the Slack equation (Slack, 1973)

$$\kappa_l = A \frac{\bar{M}\delta\Theta^3}{\gamma^2 n^{2/3} T} \quad (2.46)$$

Here $\bar{M}$, δ , n , γ , and T are average atomic mass, cube root of volume per atom, number of atoms per unit cell, Grüneisen parameter, and absolute temperature, respectively while other factors have been predefined. The coefficient A can be further expressed as

$$A = \frac{0.5 \times 5.72 \times 10^7 \times 0.849 \gamma^2}{\gamma^2 - 0.514 \gamma + 0.228} \quad (2.47)$$

2.10 Electron Localization Function (ELF)

The probability of discovering an electron in the vicinity space of a reference electron with the same spin and location is determined by the electron localization function (ELF) (Savin et al., 1992; Silvi & Savin, 1994). According to Becke and Edgecombe (Becke & Edgecombe, 1990), the dimensionless ELF can be expressed using the following equation:

$$n(r) = \frac{1}{1 + \chi(r)} \quad (2.48)$$

where $\chi(r)$ is the ratio of localization of electron $D(r)$ to uniform electron gas $D_h(r)$. This can be expressed as:

$$\chi(r) = \frac{D(r)}{D_h(r)} \quad (2.49)$$

Here $D(r)$ and $D_h(r)$ can be further expressed as

$$D(r) = 0.5 \sum_{i=1}^n |\nabla \psi(r)|^2 - 0.125 \frac{|\nabla p(r)|}{p(r)} \quad (2.50)$$

$$D_h(r) = 0.3 (3\pi^2)^{\frac{2}{3}} p(r)^{5/3} \quad (2.51)$$

The first and second terms in Equation 2.50 correspond to the kinetic energy density and the von Weizsäcker kinetic energy density approximation, respectively.

The function $D(r)$ represents the excess kinetic energy density arising from Pauli repulsion, which decreases in regions with high electron pair localization, such as lone pairs or covalent bonds, and increases where electrons with similar spin orientations are more likely to interact. The Electron Localization Function (ELF) ranges from 0 to 1, where values close to unity (>0.7) indicate highly localized electrons, such as in bonding or lone pairs. Intermediate values (0.2–0.7) suggest metallic bonding, with 0.5 representing fully delocalized electron (Jiang et al., 2018).

CHAPTER 3
STRESS INDUCED BULK Cu_3NbX_4
(X=S, Se, Te) PROPERTIES

3

Stress induced bulk Cu_3NbX_4 (X=S, Se, Te) properties

Discussions from the previous chapter (Chapter 1) disclose the fact that CSCs are well explored regarding their PVs as well as TE applications, especially in theory under ambient conditions. Various reports using different functional outlines diverse optical band gap (OBG), which sometimes deviates extensively from experimental values. Accurate determination of OBG from electronic properties is of crucial importance, as the compounds potential applications for PV and TE materials primarily depends on it. For accurate determination of OBG for CSC, it is already discussed that applying $U=5.2$ eV to Cu-d relatively predicts closer values to experimental measurements (Kehoe et al., 2015, 2016). The U value from this literature has not been explicitly calculated but rather incorporated directly from pre-existing literature on different compounds. Also, perhaps for the same reason, the authors thus failed to implement U correction for the other transition metal-Nb. Further, U have a tendency to reorganize electronic dispersion curves, and apart from determining the band gap, it can predict diverse electronic properties for different values of U . Moreover, when semiempirical method is used for U prediction instead of *ab initio* approach, capturing modifications in on-site interaction due to variations in chemical reactions, etc., under physical change cannot be realized (Sarah et al., 2018). Therefore, underlining the lack of the rigorous study, we follow the prediction of properties using *ab initio* U approach. One of the straight forward means to perturb crystals in DFT is straining the crystal, which can be brought about by inducing pressure. Pressure at the fundamental principle can lead to the reconstruction of electronic dispersion curves resulting in band modifications, direct/indirect band gap transitions, etc. Moreover, narrowing band gaps through perturbation could improve ZT by enhancing σ while effectively lowering κ_l (Alsaleh et al., 2019; Mahan & Sofo, 1996; Thonhauser et al., 2003). Also, it is evident from experiments that pressure could

enhance TE performance and improve efficiency by a factor of ~ 10 -40 in p -Bi₂Te₃ (Ovsyannikov et al., 2008) where pressure is brought about in anvil cells in the Bridgman type and that of toroidal shape. Su, N. *et al.*, (Su et al., 2019) report PF improvement in SnSe by three folds at 22 kbar pressure by the clamp-type piston-cylinder cell method, while general trends on such properties for various materials and approaches can be found in Ref. (Morozova et al., 2019). From all this understanding, this section will primarily report bulk Cu₃NbX₄ properties under pressure by applying *ab initio* U correction as well as SOC for additional accuracy.

3.1 Employed parameters for bulk Cu₃NbX₄ (X=S, Se, Te)

The GGA based on the PAW (P. E. Blöchl, 1994; Kresse & Furthmüller, 1996a, 1996b; Kresse & Joubert, 1999) method using MedeA-VASP 5.4 (Hohenberg & Kohn, 1964; Kohn et al., 1996; Kohn & Sham, 1965) code was used for this calculation. For self-consistent field (SCF) calculations, a dense 8 x 8 x 8 k-mesh was used according to Monkhorst-Pack (Monkhorst & Pack, 1976) scheme. A planewave cut-off energy of 400 eV was used, and atoms were relaxed until the forces between adjacent atoms were smaller than 0.01 eV/Å. Energy convergence criteria of 10⁻⁶ eV and the Normal block Davidson method with linear tetrahedron method (and Blöchl correction) (Peter E. Blöchl et al., 1994) were employed. For electronic property calculations, a denser k-mesh of 12 x 12 x 12 was used for more accurate calculations with the incorporation of U simultaneously with SOC. The compounds were perturbed by applying compressive isotropic pressures up to 20 GPa in steps of 5 GPa. Dynamical stability under such pressures was tested from phonon calculations for which 10 x 10 x 10 k-mesh and cut-off energy increased to 520 eV. Mechanical properties and mechanical stability were calculated using *ab initio* approach as developed by Le Page, Y. and P. Saxe (Y. Le Page & Saxe, 2001; Yvon Le Page & Saxe, 2002). The on-site Coulomb interactions of Dudarev's rotationally invariant DFT+U (Dudarev et al., 1998) *ab initio* approach were employed as implemented in Quantum Espresso (QE) code (Cococcioni & de Gironcoli, 2005; Timrov et al., 2022), which is also PAW potential-based. With the application of pressure in the order of GPa, the lattice parameters of Cu₃NbX₄ vary significantly, which effectively modifies

the electronic properties. For the same motive, this study computes the effective U at each pressure to grasp any significant changes that might be revealed by U. The pressure-dependent U is presented in Table 3.1.

Table 3.1. Calculated *ab initio* U (in eV) values for d-orbitals.

Cu ₃ NbX ₄	Atomic-d orbitals for U	0 GPa	5 GPa	10 GPa	15 GPa	20 GPa
Cu ₃ NbS ₄	Cu	11.28	11.34	11.35	11.35	11.35
	Nb	3.10	3.12	3.13	3.14	3.14
Cu ₃ NbSe ₄	Cu	11.06	11.04	11.06	11.07	11.08
	Nb	3.19	3.19	3.19	3.19	3.19
Cu ₃ NbTe ₄	Cu	11.22	11.29	11.33	11.39	11.47
	Nb	3.17	3.20	3.20	3.20	3.20

For transport properties calculation, the DFT postprocessing tool of semiclassical Boltzmann transport equations integrated into MedeA-VASP 5.4 BoltzTraP code is employed. The wavefunctions were recalculated at k-mesh of 30x30x30 in the first Brillouin zone. Furthermore, the default CRTA of $\tau=10^{-14}$ s as well as calculated relaxation time approximation (RTA) as obtained from deformation potential theory, are assumed for investigation of the transport properties.

3.2 Structural and mechanical properties

Bulk Cu₃NbX₄ (X=S, Se, Te) at ambient as well as under stress condition of 5, 10, 15, and 20 GPa compressive isotropic pressure are presented in this chapter. The crystal structure of Cu₃NbX₄ is similar to that of Figure 2.2, and resultant strain due to applied stress is shown in Figure 3.1.

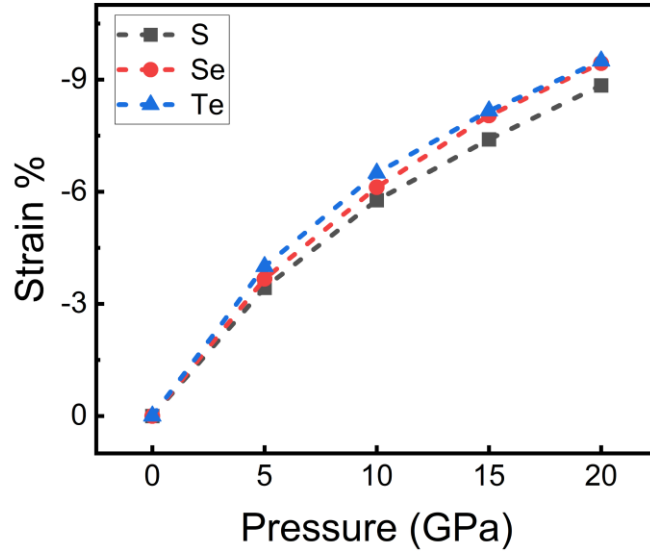


Figure 3.1. Relation of strain with applied stress for Cu_3NbX_4 ($\text{X}=\text{S}, \text{Se}, \text{Te}$). Negative strain values indicate the crystal is subjected to compressive pressure.

The cubic phase of the crystal structure is maintained with reduced lattice constant at pressures up to 20 GPa. Further, calculations are truncated at these pressures as all the three compounds under investigation are dynamically stable from phonon calculations up to these pressures, as shown in Figure 3.2, Figure 3.3, and Figure 3.4. To determine if a compound satisfies the requirements for practical synthesis, stability, durability, brittleness, etc., analysis from the elastic constant plays a crucial role (de Jong et al., 2015). In light of this, we examine the elastic constants for mechanical stability according to Mouhat *et al.*, (Mouhat & Coudert, 2014) and related results according to Equation 2.31 to Equation 2.37 are shown in Table 3.2 and Table 3.3. Predicted elastic constants and hence, various elastic moduli are in close agreement with theoretical values of similar exchange-correlation functional (Ali et al., 2014; Hong et al., 2017; Li et al., 2019). The following is how the Born requirements for mechanical stability are determined (Born, 1940):

$$C_{11}-C_{12} > 0; C_{11}+2C_{12} > 0; C_{44} > 0 \quad (3.1)$$

With the influence of pressure, Equation 3.1 can be modified according to Sin'ko *et al.*, (Sin'ko & Smirnov, 2004) as

$$\tilde{C}_{11} > 0, \tilde{C}_{11} > |\tilde{C}_{12}|, \tilde{C}_{44} > 0, \tilde{C}_{11} + 2\tilde{C}_{12} > 0 \quad (3.2)$$

where

$$\tilde{C}_{11} = C_{11} - P, \tilde{C}_{12} = C_{12} + P, \tilde{C}_{44} = C_{44} - P, (P \rightarrow \text{applied pressure}) \quad (3.3)$$

Table 3.2. Computed lattice parameter $a(\text{\AA})$, elastic constants C_{11} , C_{12} , and C_{44} (GPa) for Cu_3NbX_4 at 0, 5, 10, 15, and 20 GPa isotropic pressure.

Cu_3NbX_4	GPa	a	C_{11}	C_{12}	C_{44}
Cu_3NbS_4	0	5.54	93.08	10.11	28.05
	5	5.35	126.64	25.74	29.85
	10	5.22	158.12	40.79	31.57
	15	5.13	184.66	54.32	25.20
	20	5.05	211.26	69.76	26.68
Cu_3NbSe_4	0	5.72	79.23	15.34	25.47
	5	5.51	117.51	39.44	29.18
	10	5.37	143.87	54.64	27.51
	15	5.26	174.35	72.80	31.88
	20	5.18	199.10	87.82	35.63
Cu_3NbTe_4	0	6.00	62.27	16.54	32.34
	5	5.76	91.65	34.13	30.82
	10	5.61	122.86	56.15	38.09
	15	5.51	154.44	80.23	43.31
	20	5.43	177.69	97.03	46.47

Table 3.3. Deduced mechanical properties according to Hill's approximation from elastic constants C_{11} , C_{12} , and C_{44} : Bulk modulus B, Shear modulus G, and Young's modulus Y (GPa), dimensionless Poisson's ratio ν , Pugh's ratio B/G, the Gruneisen parameter γ , and Debye temperature Θ_D (Kelvin) for Cu_3NbX_4 at 0, 5, 10, 15 and 20 GPa isotropic pressure.

Cu_3NbX_4	GPa	B	G	Y	ν	B/G	γ	Θ_D
Cu_3NbS_4	0	37.77	32.83	76.35	0.16	1.15	1.1547	337.5
	5	59.38	36.88	91.65	0.24	1.61	1.4655	359.7
	10	79.90	40.57	104.06	0.28	1.97	1.6714	377.0
	15	97.77	37.29	99.15	0.33	2.62	1.9811	361.9
	20	116.92	39.92	107.40	0.35	2.93	2.1047	373.3
Cu_3NbSe_4	0	36.63	27.89	66.74	0.20	1.31	1.2720	263.0
	5	65.46	32.79	84.29	0.28	2.00	1.6857	286.3
	10	84.38	33.42	88.56	0.33	2.52	1.9395	288.8
	15	106.65	38.45	102.96	0.34	2.77	2.0439	308.4
	20	124.92	42.63	114.81	0.35	2.93	2.1053	323.5
Cu_3NbTe_4	0	31.79	28.15	65.19	0.16	1.13	1.1388	234.2
	5	53.30	29.98	75.73	0.26	1.78	1.5655	243.3
	10	78.39	36.12	93.93	0.30	2.17	1.7744	266.3
	15	104.97	40.71	108.16	0.33	2.58	1.9626	281.8
	20	123.92	43.91	117.81	0.34	2.82	2.0631	291.8

It is noticeable from Table 3.2 that the elastic constants satisfy all the necessary and sufficient conditions for mechanical stability indicating their stability towards elastic deformations. According to our estimates, under large compressive stresses, the B value dramatically rises according to Equation 2.33 as C_{11} and C_{12} drastically escalate. Similar conclusions, however, cannot be drawn in G, as all the three independent parameters of C_{11} , C_{12} , and C_{44} are correlated into Equation 2.32. All this result suggests that Cu_3NbX_4 will not fracture or deform plastically at such high compressive pressure. The Young's modulus (Y), which indicates the stiffness of a material, also tends to increase with pressure for our compounds. The Cu_3NbX_4 under investigation have their respective ν and B/G ratios less than the critical limit of 0.28 and 1.75, indicating their brittleness, which is consistent with existing literature (Haque, 2021; Taghizade et al., 2019). However, as pressure is induced, their values begin to rise linearly and increase beyond critical limit after a certain pressure relative to the compound. Also, for predicting melting temperatures (T_m) of the compounds, the expression $T_m = 553 + 5.91C_{11}$ was implemented according to Fine *et al.*, (Fine et al., 1984) and is obtained to be 901K, 1001K, and 1083K, respectively, for X=Te, Se, and S. Cu_3NbS_4 exhibits a minimum strain-to-pressure ratio, followed by Cu_3NbSe_4 and Cu_3NbTe_4 , indicating difficulty to volume change. This idea can also be grasped from their Bulk modulus 'B' value, which mainly depends on C_{11} in their pristine states (at 0 GPa) where B indicates resistance towards volume change due to external deformations. Consequently, Cu_3NbS_4 , possessing a comparatively higher B value, displays minimum strain due to pressure, followed by Cu_3NbSe_4 and Cu_3NbTe_4 , as expected.

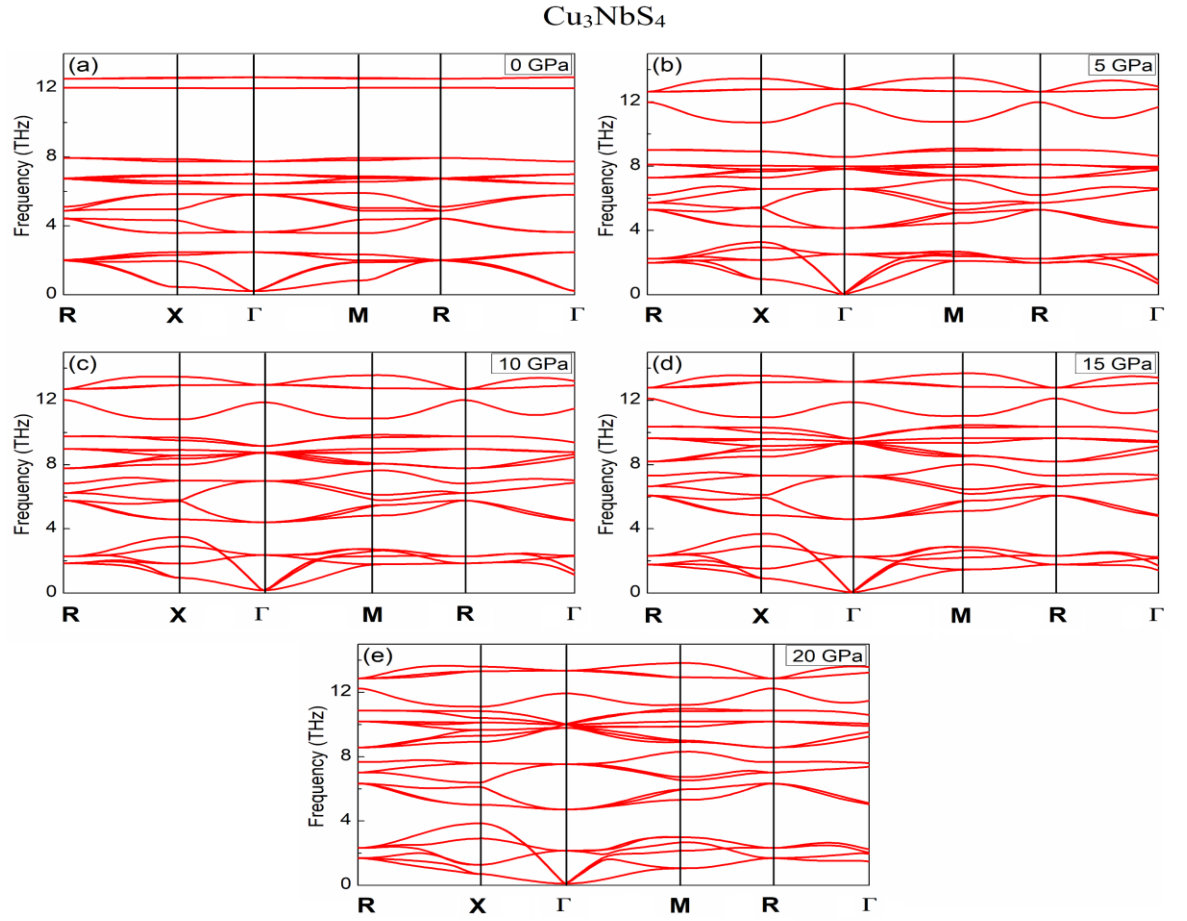


Figure 3.2. Phonon dispersion curves of Cu_3NbS_4 at (a) 0, (b) 5, (c) 10, (d) 15, and (e) 20 GPa pressure. Absence of negative phonon frequencies indicates dynamical stability of the compounds for favourable synthesis of the compounds.

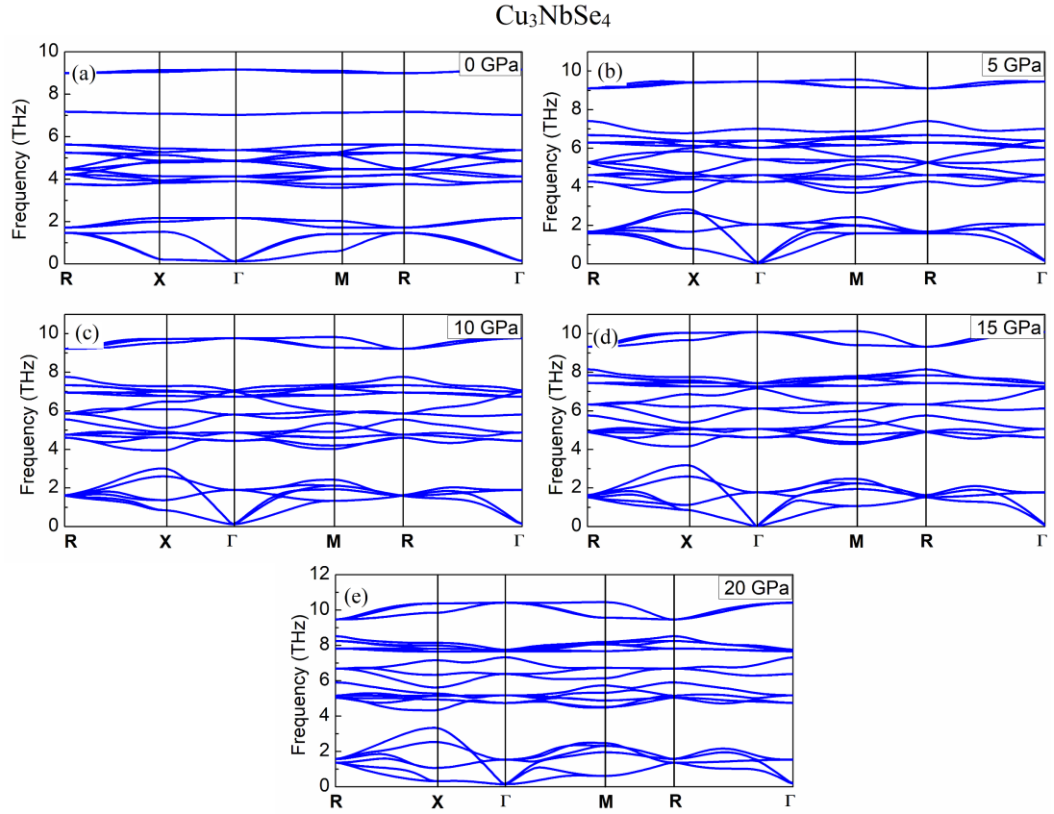


Figure 3.3. Phonon dispersion curves of Cu_3NbSe_4 at (a) 0, (b) 5, (c) 10, (d) 15, and (e) 20 GPa pressure. Absence of negative phonon frequencies indicates dynamical stability of the compounds for favourable synthesis of the compounds.

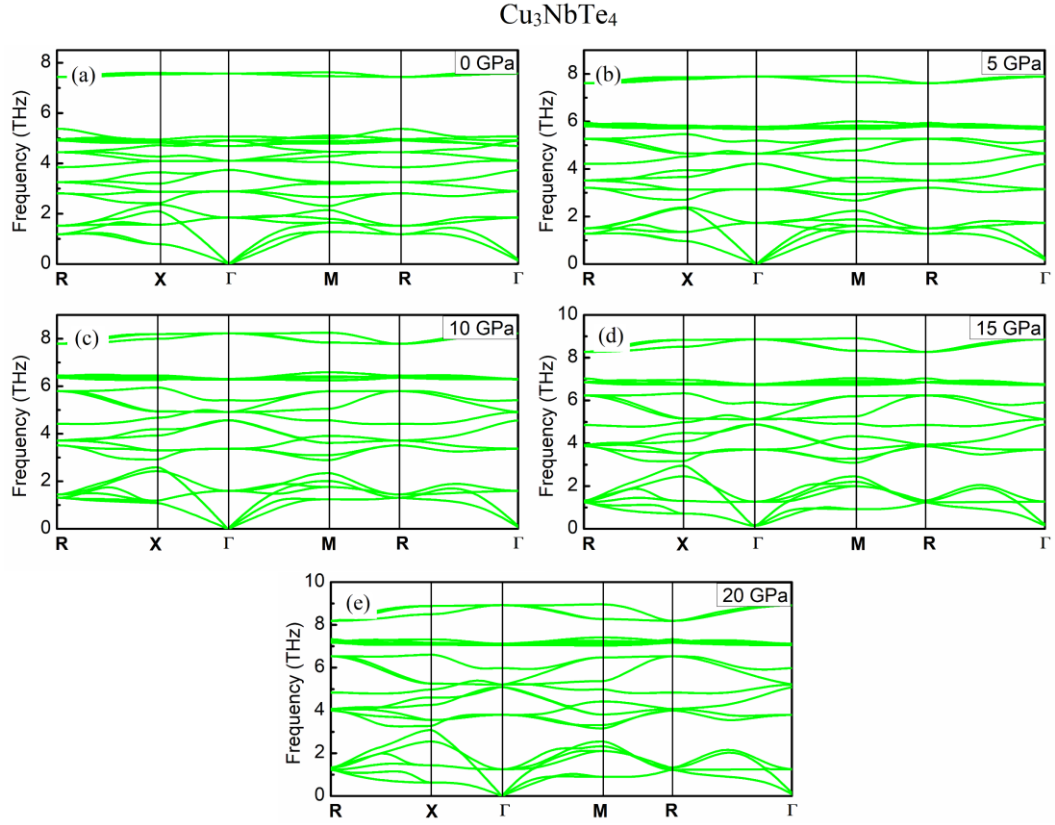


Figure 3.4. Phonon dispersion curves of Cu_3NbTe_4 at (a) 0, (b) 5, (c) 10, (d) 15, and (e) 20 GPa pressure. Absence of negative phonon frequencies indicates dynamical stability of the compounds for favourable synthesis of the compounds.

3.3 Electronic properties

The estimation of band gaps comparable to experimental values is one of the main emphases and challenges in DFT. Especially for semiconductors, the band gap largely aids in speculating applicability for certain applications and device fabrication, etc. Further, for this study, where the focus is on optoelectronic and TE applications, band gaps play a crucial role because, beyond certain limits, the compounds could be rendered less efficient or completely impractical for such applications.

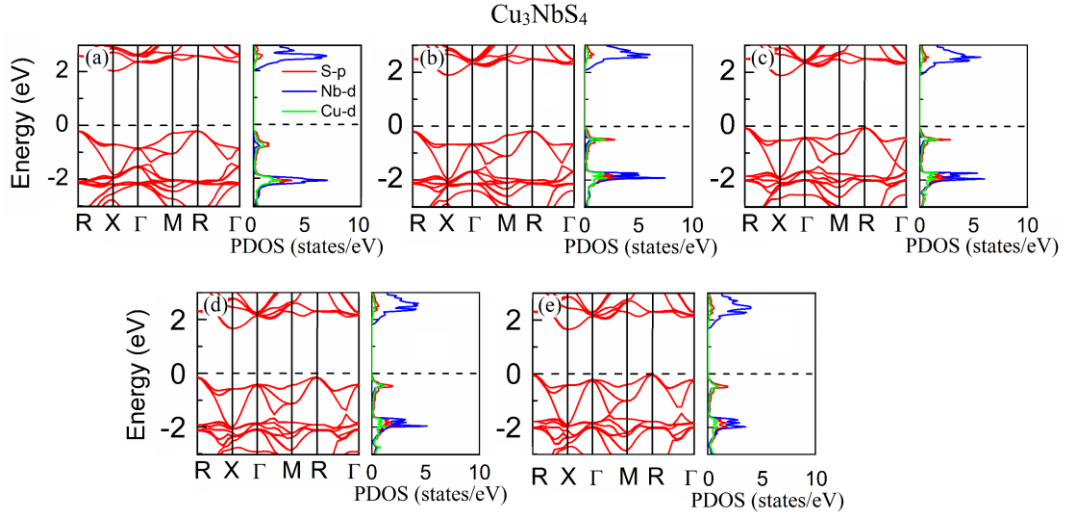


Figure 3.5. Band structure and their corresponding DOS for Cu_3NbS_4 (a) 0, (b) 5, (c) 10, (d) 15, and (e) 20 GPa pressure, revealing the reduction in band gaps with pressure.

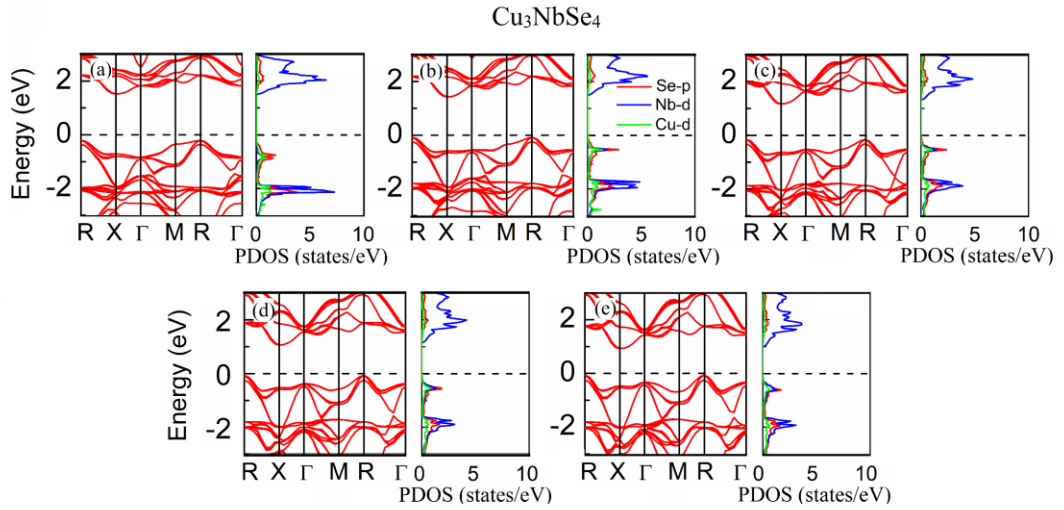


Figure 3.6. Band structure and their corresponding DOS for Cu_3NbSe_4 at (a) 0, (b) 5, (c) 10, (d) 15, and (e) 20 GPa pressure, revealing the reduction in band gaps with pressure.

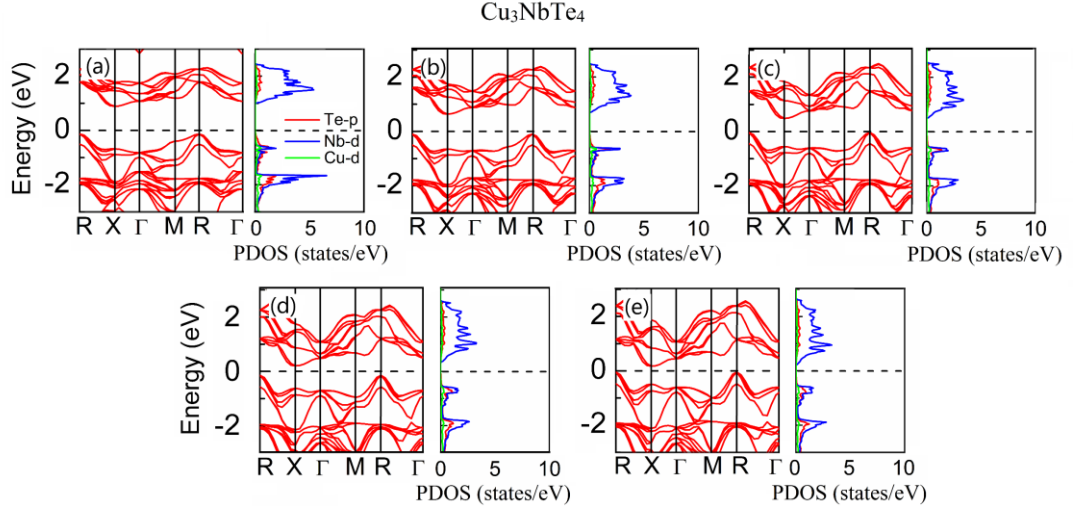


Figure 3.7. Band structure and their corresponding DOS for Cu_3NbTe_4 at (a) 0, (b) 5, (c) 10, (d) 15, and (e) 20 GPa pressure, revealing the reduction in band gaps with pressure.

The electronic band structures along R-X- Γ -M-R- Γ high symmetry points with corresponding partial density of states (PDOS) calculated using GGA+U+SOC for Cu_3NbX_4 at 0, 5, 10, 15, and 20 GPa are presented in Figure 3.5, Figure 3.6, and Figure 3.7. The variation of energy band gaps with pressure is presented in Table 3.4. Conclusion can be drawn that Cu_3NbX_4 are indirect band gap semiconductors with decreasing energy band gaps down the chalcogenide groups, which is consistent with literature from theory as well as experiments. The valence band maximum (VBM) and conduction band minimum (CBM) are located at the R and X symmetry points of the first Brillouin zone, respectively. It is also observed that the effect of SOC increases down the chalcogenide groups, which is appreciable due to the introduction of successively heavier atoms. Almost no significant band splitting occurs in Cu_3NbS_4 , while maximum splitting is observed for the heaviest Cu_3NbTe_4 compound, with an intermediate effect occurring for Cu_3NbSe_4 . Furthermore, band splitting due to SOC occurs along the high symmetry point R with split-off energy in the order $\text{Cu}_3\text{NbS}_4 < \text{Cu}_3\text{NbSe}_4 < \text{Cu}_3\text{NbTe}_4$, where split-off energy due to SOC is completely absent in Cu_3NbS_4 . From PDOS analysis, d-orbitals of Nb persist as the main contributor to the conduction band (CB) near the Fermi level $E_F (= 0 \text{ eV})$ with minor

contributions from possible hybridized states of X-p and Cu-d orbitals. In the valence band (VB) all possible hybridized states from p-orbitals of chalcogenide atoms, Nb-d and Cu-d orbitals contribute near the E_F while Cu-d orbitals persist to be the dominant contributor in the deeper energy bands (~ -4 eV).

Upon inducing pressure, the fundamental band gap decreases congruently, wherein for Cu_3NbS_4 , Cu_3NbSe_4 , and Cu_3NbTe_4 , the gaps fall in the range 2.23-1.67 eV, 1.72-0.99 eV, and 1.02-0.22 eV, respectively. This diminishing band gap with pressure suggests enhanced optoelectronics as well as TE properties as a consequence that lower energy ranges can be utilized beneficially, which was otherwise directly excluded when the compound possesses larger energy band gaps at ambient pressure. The narrowing of band gaps is due to the modification in the dispersion curves where energy bands from the CB are pushed towards the E_F . The orbital contributors to energy bands under pressure are identical to 0 GPa with a narrowing of the gap between the VB and CB in congruence with the electronic dispersion bands.

Table 3.4. Variation of energy band gaps (eV) with pressure for Cu_3NbX_4 (X=S, Se and Te).

Cu_3NbX_4	0 GPa	5 GPa	10 GPa	15 GPa	20 GPa
Cu_3NbS_4	2.23, 1.65♥, 2.66♦, 1.82♠	2.08	1.94	1.81	1.67
Cu_3NbSe_4	1.72, 2.20♦, 1.45♠	1.50	1.31	1.14	0.99
Cu_3NbTe_4	1.02, 0.92♠, 1.62♦	0.74	0.52	0.35	0.22

♠→(Kehoe et al., 2016), ♦→(Espinosa-García et al., 2018)

♥→(Taghizade et al., 2019)

3.4 Optical properties

The examination of optical characteristics helps to understand how materials interact with incident radiation. The obtained optical characteristics of Cu_3NbX_4 are isotropic along the three axes due to their cubic structure. The computed results for optical properties following Equation 2.38 to Equation 2.43 are plotted for $\epsilon(\omega)$ at 0, 5, 10, 15, and 20 GPa for Cu_3NbX_4 (X=S, Se, Te) in Figure 3.8, Figure 3.9, and Figure 3.10. It can be generalised that optical activity increases down the chalcogenide groups for Cu_3NbX_4 . Interestingly, a significant portion of optical activity falls within the visible range, which is ideal for PV applications. At ambient pressure, static dielectric constants ϵ_1 are 6.5, 7.5, and 10.2 respectively for Cu_3NbX_4 down the chalcogenide groups, which gradually increases with the energy of incident radiation, reached the first peak in the visible range and then decreases again. This high ϵ_1 is quite desirable for solar PVs as materials with such properties tend to decrease charge carrier recombination rates. Negative $\epsilon_1(\omega)$ observed in certain photon energy ranges indicates metallic reflectivity in that region, disclosing additional potential applications in wave absorbing, wave transmission in antennas, electromagnetic radiation shields, etc (Balun et al., 2020; Lee & Heeger, 2003). From the plot of $\epsilon_2(\omega)$, it can be seen that optical activity ceases to exist until certain incident radiation. Optical activity edge (OAE), which can be defined as the onset when $\epsilon_2(\omega) > 0$, in general, is maximum in S-based CSCs, decreases for Se and the least for Te compounds. On the onset of OAE, $\epsilon_2(\omega)$ rapidly increase some falling in the visible range, especially for Cu_3NbTe_4 , suggesting potential optoelectronics. When pressure is induced, optical properties are enhanced, especially in the IR-vis range. $\epsilon_1(\omega)$ subsequently increases for the three compounds until certain energy region and red shifting in their respective peaks. Due to the same, the onset of metallic reflectivity is red-shifted, particularly for Cu_3NbTe_4 ; reflection could occur at around ~ 3.0 eV, signifying their effectiveness for blue-UV light reflectors. The same pressure also correspondingly causes the imaginary part $\epsilon_2(\omega)$ of dielectric function to red shift in their optical peaks as well as in their OAE. This once more suggests stronger activity (perhaps absorption, etc.) in the visible energy spectrum, pointing towards prospects for potential solar PVs.

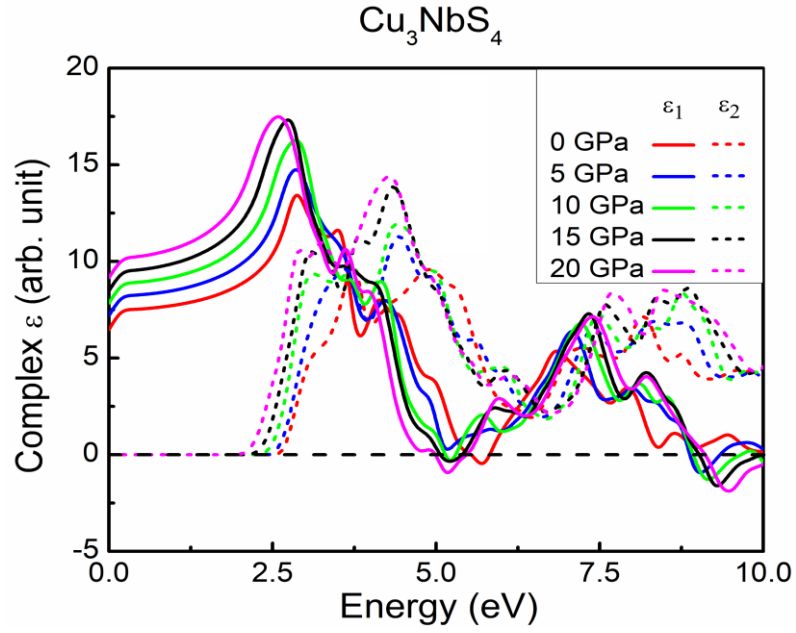


Figure 3.8. Predicted complex dielectric function (ϵ) in arbitrary units for Cu_3NbS_4 at 0, 5, 10, 15, and 20 GPa pressure, demonstrating red shifting in optical activity with pressure for enhanced optical properties.

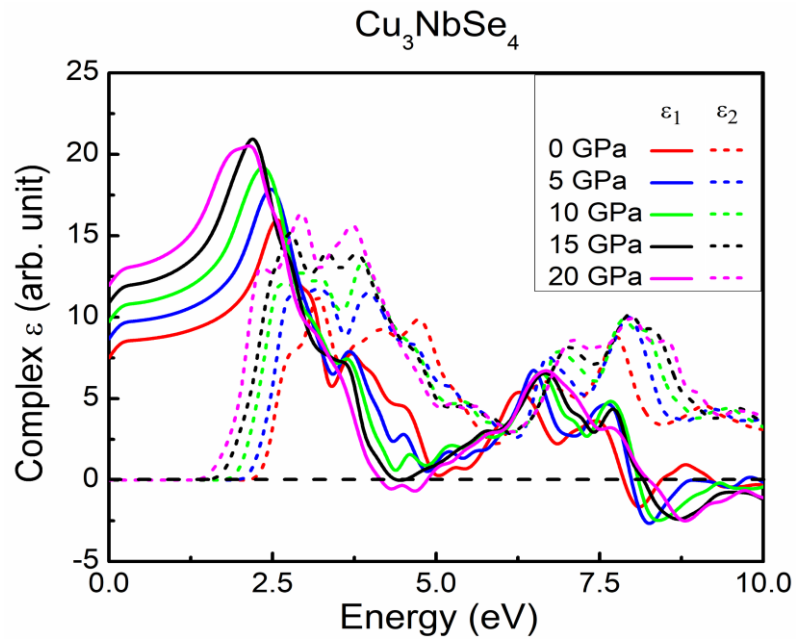


Figure 3.9. Predicted complex dielectric function (ϵ) in arbitrary units for Cu_3NbSe_4 at 0, 5, 10, 15, and 20 GPa pressure, demonstrating red shifting in optical activity with pressure for enhanced optical properties.

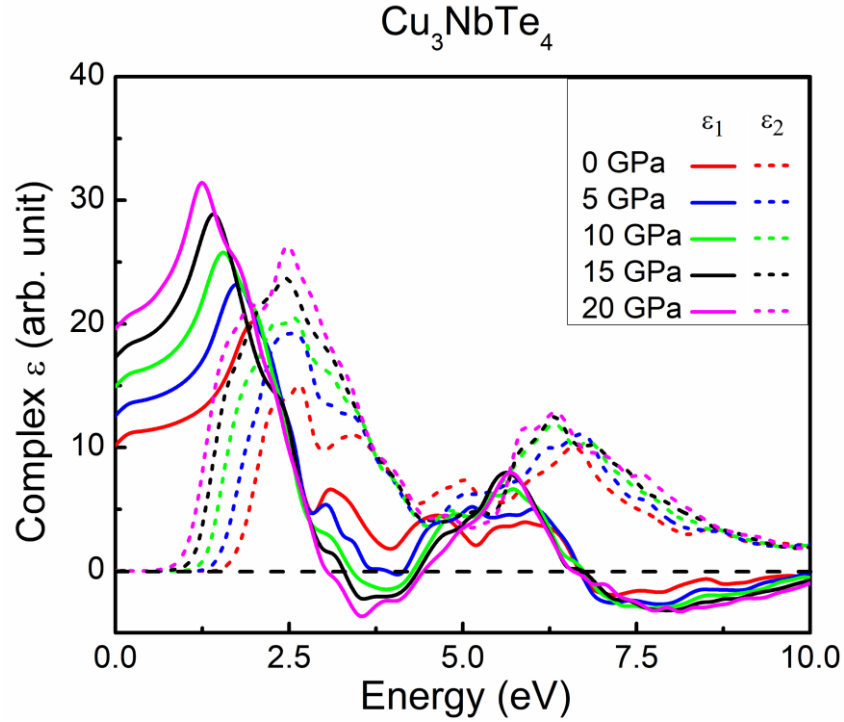


Figure 3.10. Predicted complex dielectric function (ϵ) in arbitrary units for Cu_3NbTe_4 at 0, 5, 10, 15, and 20 GPa pressure, demonstrating red shifting in optical activity with pressure for enhanced optical properties.

For the three Cu_3NbX_4 compounds, concerning change in photon energy, η increases and reaches its maximum value at $\sim 2.89\text{--}2.07$ eV down the chalcogenide groups, after which it abruptly falls again. Normal dispersion is elucidated by the rise in η with increasing incident energy, whereas anomalous dispersion is indicated by a drop in η with rising energy. Since anomalous dispersion frequently happens in areas with high radiation absorption, it is of distinct importance for this study. The k is maintained at zero up to a certain energy range with sudden optical activity at $\sim 1.68\text{--}2.68$ eV, indicating the onset of energy-related interaction from that range. The absorption coefficient (α) can be better for interpreting the loss of photon energy during media propagation; the functional change in k is thus correlated with α and will be covered in the next section. With pressures of 5, 10, 15, and 20 GPa, η not only amplifies with photon energy but also redshifts in its peak position. This indicates that applying pressure can cause the onset of anomalous dispersion to shift to lower photon energy, directing enhanced radiation absorption toward the visible range. It can be

noted that η and k curves overlap for the same energy range as $\epsilon_1(\omega) < 0$, depicting the same total reflection in the region as shown in Figure 3.11, Figure 3.12, and Figure 3.13.

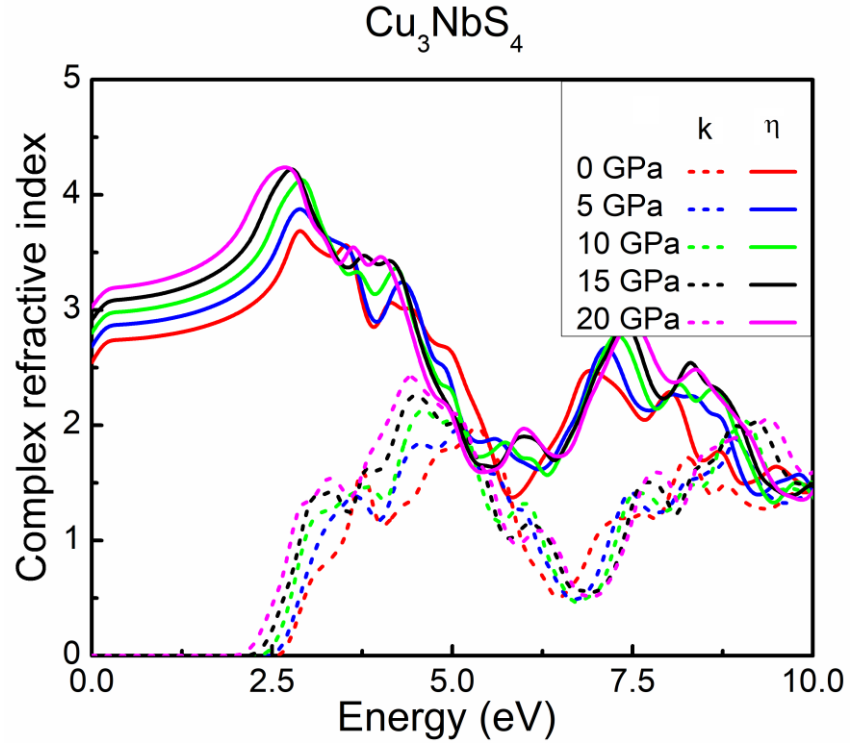


Figure 3.11. Deduced extinction coefficient (k) and refractive index (η) for Cu_3NbS_4 at 0, 5, 10, 15, and 20 GPa pressure.

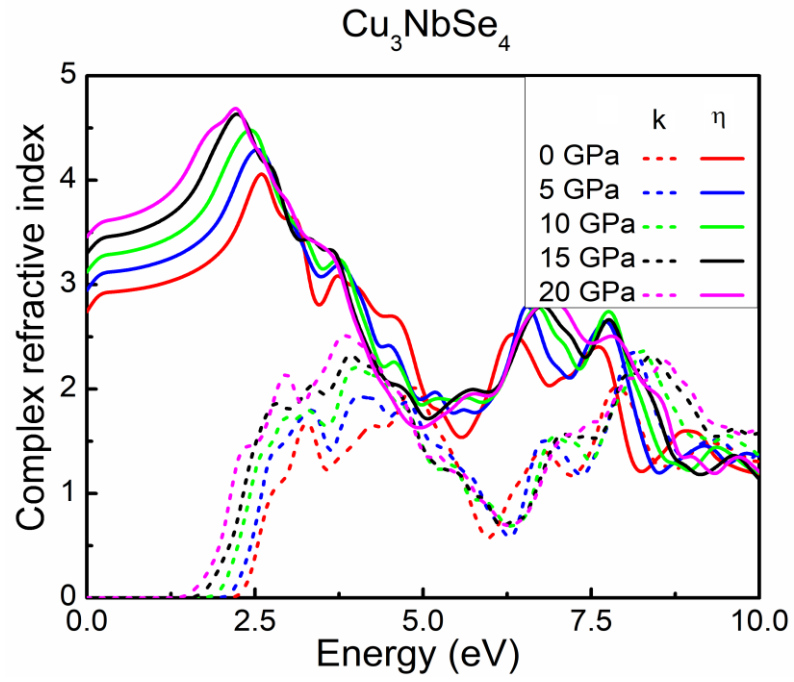


Figure 3.12. Deduced extinction coefficient (k) and refractive index (η) for Cu_3NbSe_4 at 0, 5, 10, 15, and 20 GPa pressure.

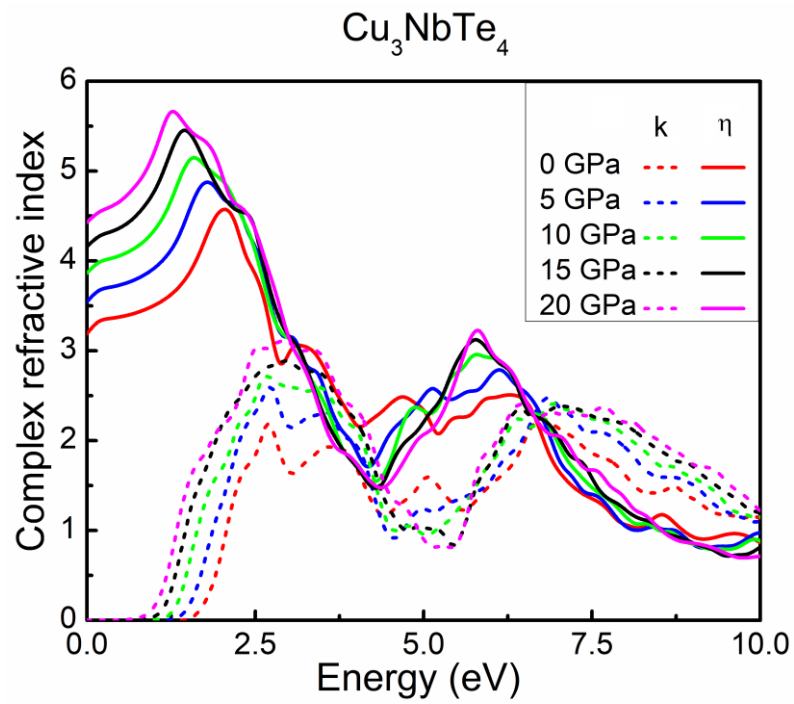


Figure 3.13. Deduced extinction coefficient (k) and refractive index (η) for Cu_3NbTe_4 at 0, 5, 10, 15, and 20 GPa pressure.

The plot of α against incident photon energy is shown in Figure 3.14, Figure 3.15, and Figure 3.16. Since most solar PVs operate in the IR-vis-UV spectrum upper energy limit of 5 eV is considered. For Cu_3NbS_4 , Cu_3NbSe_4 , and Cu_3NbTe_4 , the absorption edge occurs at 2.69, 2.34, and 1.84 eV, respectively at 0 GPa. This is above the energy band gap determined from electronic band structures, indicating that the compounds are indeed indirect band gap semiconductors. Even under ambient pressure, Cu_3NbX_4 exhibits good optical absorption in the order of 10^5 cm^{-1} throughout the photon energy range. Prominent peaks in the visible range (up to $\sim 3 \text{ eV}$) are correspondingly observed at 1.89×10^5 , 3.58×10^5 , and $5.96 \times 10^5 \text{ cm}^{-1}$, respectively. Optical absorptions are further enhanced under applied pressure, the first observation being red shifting in absorption edge, and secondly shifting of absorption peaks towards the lower energy spectrum. Red shifting in absorption edge to 2.21, 1.82, and 1.07 eV (at 20 GPa for reference) is advantageous because lower photon energy can now be absorbed, thus enhancing the PV's performance. Moreover, corresponding absorption peaks in the visible range are respectively enhanced for the same photon energy 4.12×10^5 , 6.48×10^5 , and $9.40 \times 10^5 \text{ cm}^{-1}$ (at 20 GPa for reference), indicating enhanced photon absorption under pressure. These results indicate that pressure has a promising effect on the prospects of Cu_3NbX_4 as absorbing material by simultaneously broadening the photon energy absorption range and magnitude in absorption coefficient.

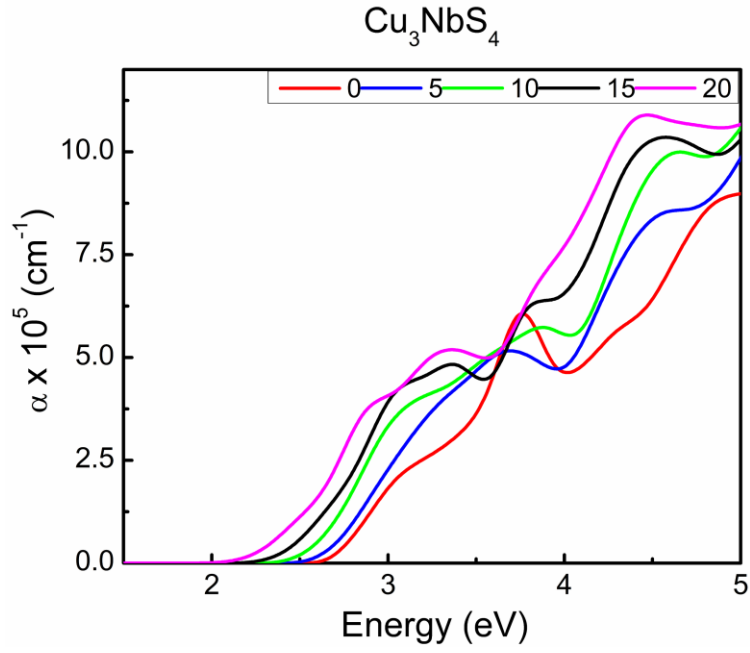


Figure 3.14. Deduced absorption coefficient (α) $\times 10^5$ cm^{-1} for Cu_3NbS_4 at 0, 5, 10, 15, and 20 GPa pressure demonstrating enhanced optical absorption coefficient and red shifting with pressure.

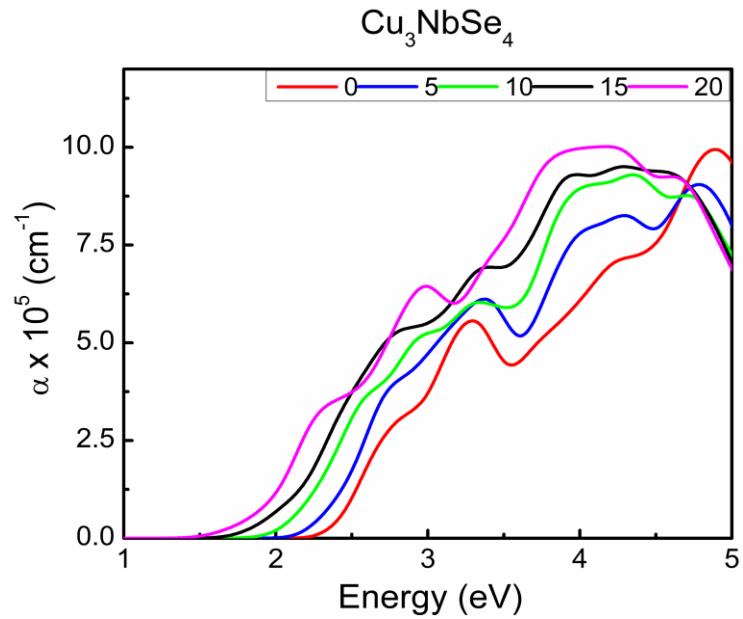


Figure 3.15. Deduced absorption coefficient (α) $\times 10^5$ cm^{-1} for Cu_3NbSe_4 at 0, 5, 10, 15, and 20 GPa pressure demonstrating enhanced optical absorption coefficient and red shifting with pressure.

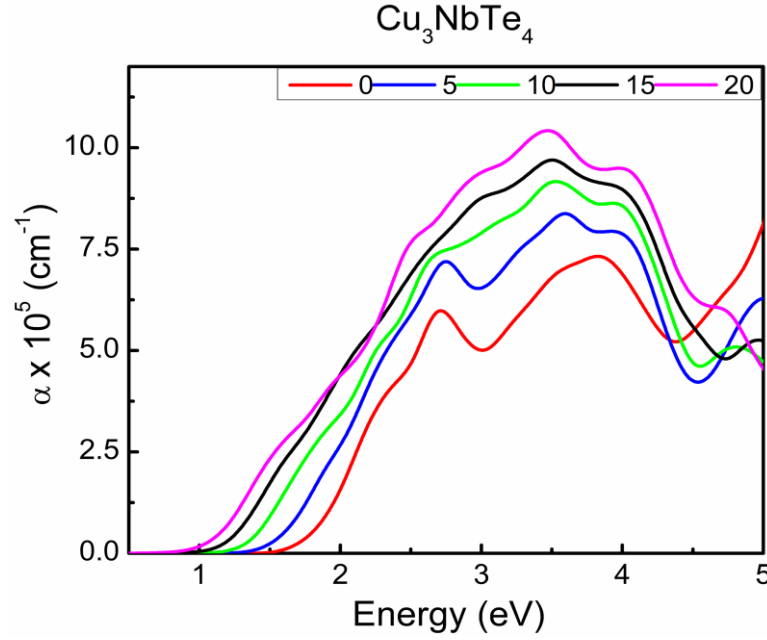


Figure 3.16. Deduced absorption coefficient (α) $\times 10^5 \text{ cm}^{-1}$ for Cu_3NbTe_4 at 0, 5, 10, 15, and 20 GPa pressure demonstrating enhanced optical absorption coefficient and red shifting with pressure.

Corresponding OBG, along with other optical parameters are presented in Table 3.4. At 0 GPa, the direct OBG (E_g^{opt}) for Cu_3NbS_4 and Cu_3NbSe_4 are predicted to be 2.74 and 2.41 eV, respectively, which is in good agreement with experimental band gaps. Consequently, our predicted OBG of 1.85 eV could be contemplated as accurate in the absence of experimental evidence for Cu_3NbTe_4 . The OBGs consequently decrease with pressure as already projected by ϵ_2 and η , resulting in E_g^{opt} to vary from 2.74 to 1.28 eV for the compounds. This expresses that E_g^{opt} could be favourably tuned to the aforementioned desired range for potential optoelectronics applications.

Table 3.5. Optical band gaps E_g^{opt} (eV), real part of static dielectric function ϵ_1 , refractive index η at 0 eV, and peak absorption α in the visible range (cm^{-1}).

Cu_3NbX_4	GPa	E_g^{opt}	$\epsilon_1(\omega)$	η	$\alpha \times 10^5$
Cu_3NbS_4	0	2.74, 2.50 ^{*♥} , 2.60 ^{*♦} , 2.56 ^{*♠} , 3.47 [♣] , 3.21 [♠] , 2.31 [‡]	6.58	2.56	1.89
	5	2.70	7.29	2.71	2.36
	10	2.59	7.96	2.82	3.40
	15	2.51	8.62	2.92	3.99
	20	2.39	9.21	3.03	4.12
Cu_3NbSe_4	0	2.41, 2.45 ^{*†} , 2.20 ^{*♦} , 2.13 ^{*♠} , 2.64 [♣] , 2.75 [♠] , 1.95 [‡]	7.54	2.75	3.58
	5	2.32	8.87	2.96	4.79
	10	2.15	9.84	3.12	5.25
	15	2.09	11.01	3.32	5.51
	20	1.93	11.95	3.47	6.48
Cu_3NbTe_4	0	1.85, 1.46 [‡] , 2.24 ^{*♠} , 1.08 [‡]	10.34	3.18	5.96
	5	1.68	12.74	3.56	7.20
	10	1.52	15.12	3.86	7.90
	15	1.37	17.44	4.19	8.80
	20	1.28	19.64	4.43	9.40

* $\rightarrow$ Experiment. $\dagger \rightarrow$ (Grima-Gallardo et al., 2016) $\ddagger \rightarrow$ (Hong et al., 2017) $\clubsuit \rightarrow$ (Kehoe et al., 2016) $\downarrow \rightarrow$ (Kehoe et al., 2015) $\rightarrow \spadesuit \rightarrow$ (Espinosa-García et al., 2018) $\blackspadesuit \rightarrow$ (Hersh, 2007) $\blacklozenge \rightarrow$ (E. M. Chen et al., 2017) $\heartsuit \rightarrow$ (Ikeda et al., 2019)

3.5 Thermoelectric properties

The semiclassical Boltzmann transport theory proposes that electrons obey classical equations of motion between scattering events separated by a relaxation time while relying on the quantum-mechanical calculation of the electronic states. Within the CRTA as well as RTA according to BoltzTraP code, this work presents transport coefficients such as the Seebeck coefficient (S), which is the potential difference generated when two ends of a TE material are maintained at different temperatures, electrical conductivity (σ), total thermal conductivity (κ_T), which is determined by two parts: the electronic part (κ_e) and the lattice part (κ_l), TE power factor (PF), and TE figure of merit (ZT). Based on the semi-classical Boltzmann theory as implemented in BoltzTraP code, the TE parameters are computed.

Making use of Equation 2.44, Equation 2.45, and Equation 2.46, for easier comparison, S , σ , and κ_e are initially computed within the CRTA ($\tau = 10^{-14}$ s) as illustrated in Figure 3.17, Figure 3.18, and Figure 3.19. Electronic properties calculation already reveals a decrease in band gaps for $X=S>Se>Te$ as well as with pressure. For this same reason, Cu_3NbX_4 thus exhibits intensifying σ and κ_e while reduced S value with diminishing band gaps as expected. The Seebeck coefficient S is observed to vary in magnitude in the order $X=S>Se>Te$ and is inversely proportional to temperature. The decrease in S from 2000-1000 $\mu V K^{-1}$ down the chalcogenide group can be understood from the gradual decrease in their band gaps. Further, the investigated compounds are observed to exhibit high σ in the order of 10^6 - 10^5 $S m^{-1}$. The electronic part of thermal conductivity κ_e is observed to show moderate values which could be beneficial for TE materials and is directly proportional to temperature. The proportionality with temperature is comprehensible that charge carriers possess more kinetic energy leading to an upsurge in magnitude. Pressure has a significant impact on all the aforementioned transport properties, which vary depending on whether band gaps increase or decrease with pressure in general. Finally, the power factor PF against chemical potential is presented in Figure 3.20, Figure 3.21, and Figure 3.22. using Equation 20 with negative μ depicting p-type doping while positive μ for n-type doping.

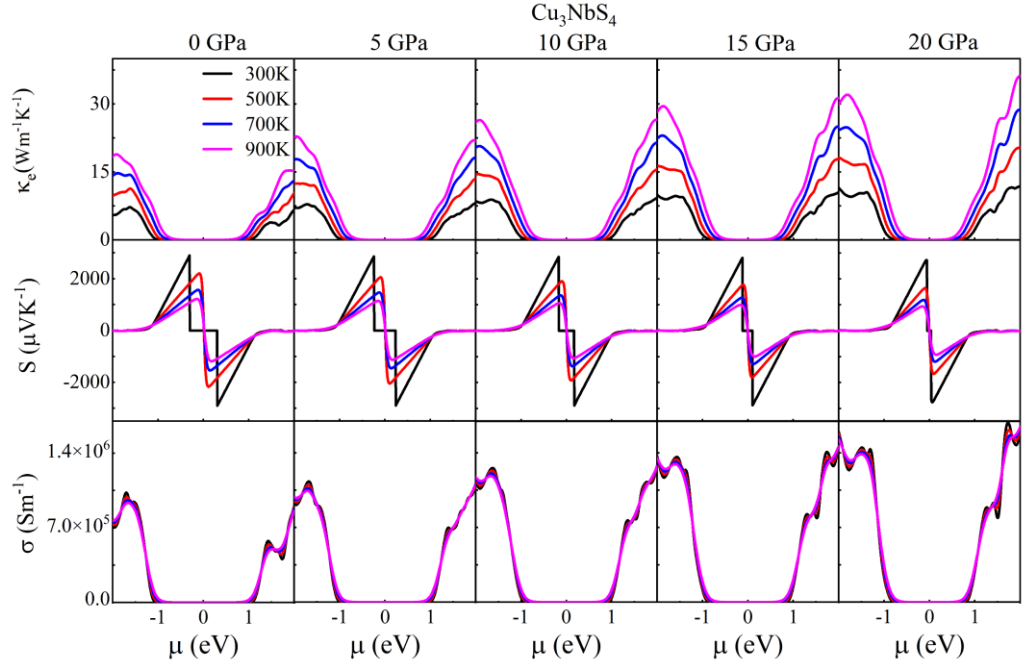


Figure 3.17. Calculated electronic part of thermal conductivity (κ_e), Seebeck coefficient (S), and electrical conductivity (σ) for Cu_3NbS_4 at 0, 5, 10, 15, and 20 GPa pressure within CRTA.

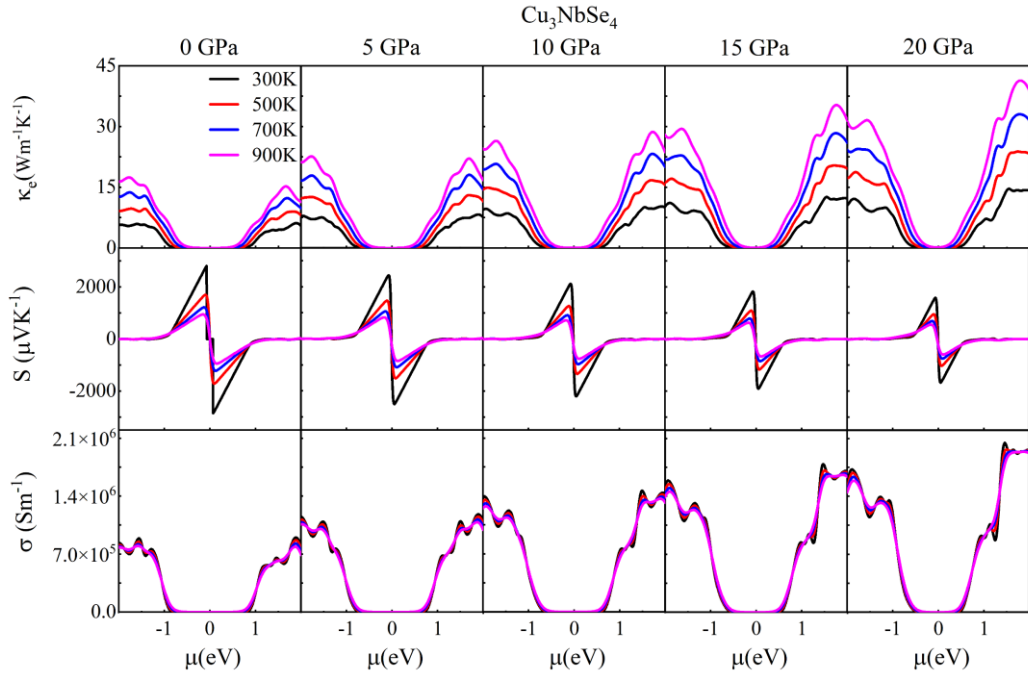


Figure 3.18. Calculated electronic part of thermal conductivity (κ_e), Seebeck coefficient (S), and electrical conductivity (σ) for Cu_3NbSe_4 at 0, 5, 10, 15, and 20 GPa pressure within CRTA.

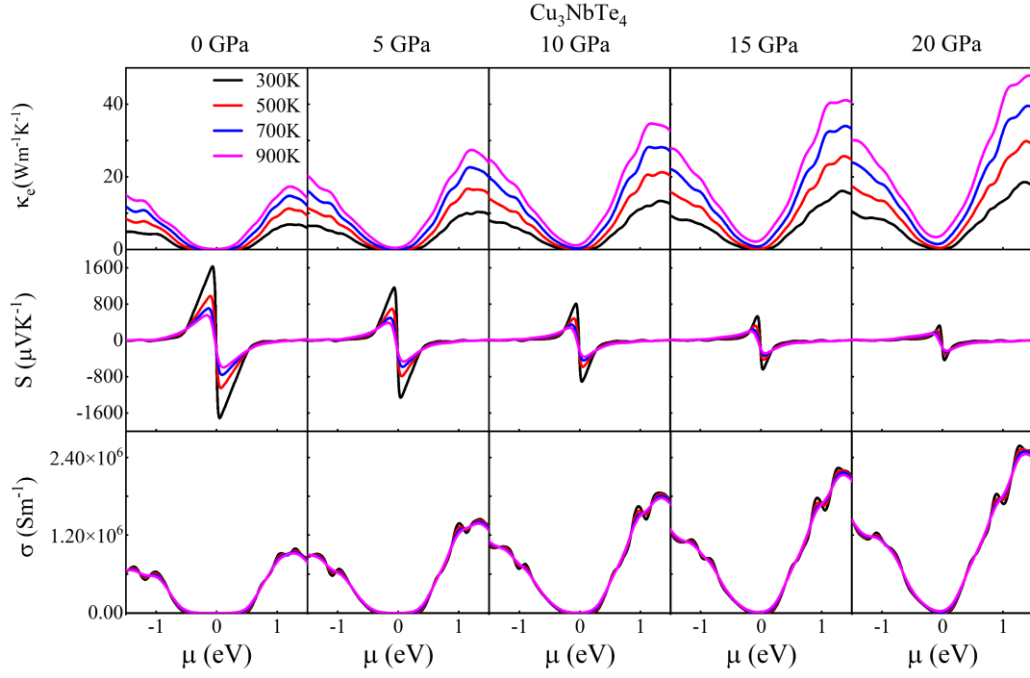


Figure 3.19. Calculated electronic part of thermal conductivity (κ_e), Seebeck coefficient (S), and electrical conductivity (σ) for Cu_3NbS_4 at 0, 5, 10, 15, and 20 GPa pressure within CRTA.

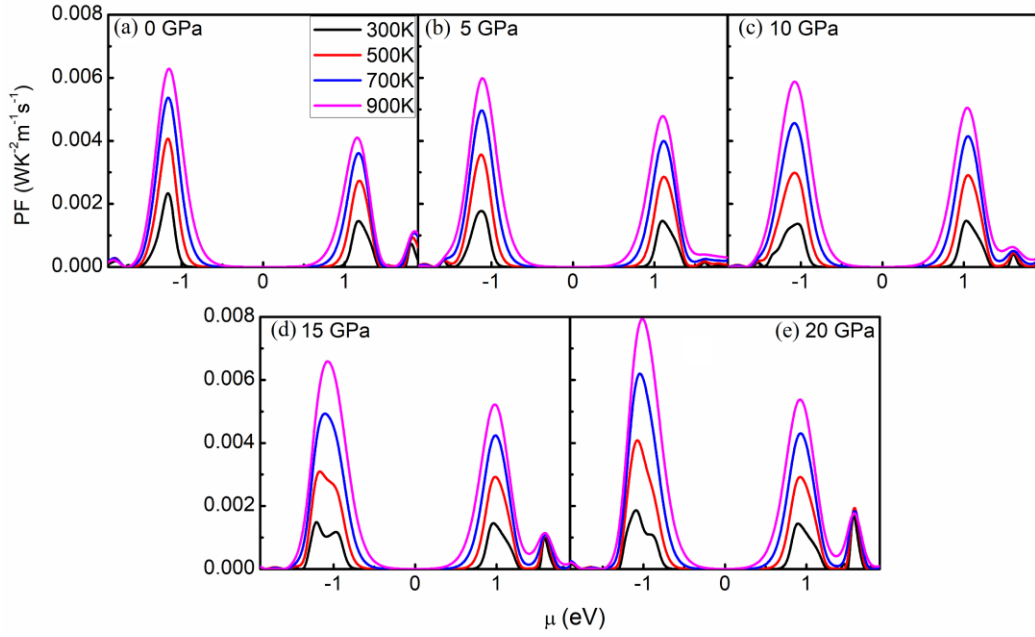


Figure 3.20. Plot of power factor (PF) for Cu_3NbS_4 at (a) 0, (b) 5, (c) 10, (d) 15, and (e) 20 GPa pressure within CRTA.

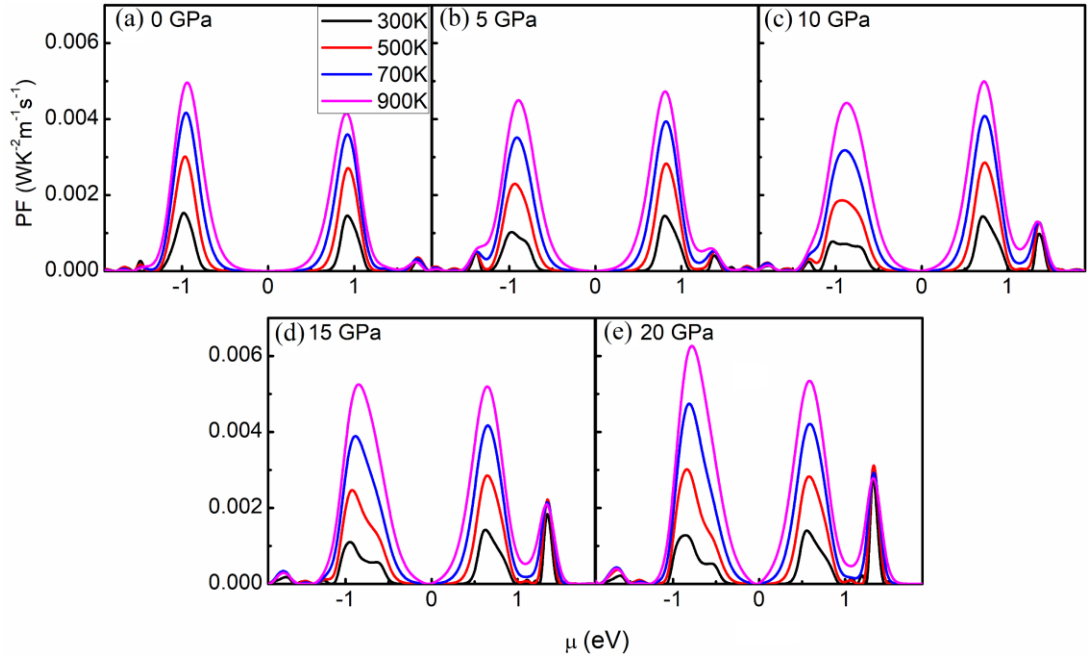


Figure 3.21. Plot of power factor (PF) for Cu_3NbSe_4 at (a) 0, (b) 5, (c) 10, (d) 15, and (e) 20 GPa pressure within CRTA.

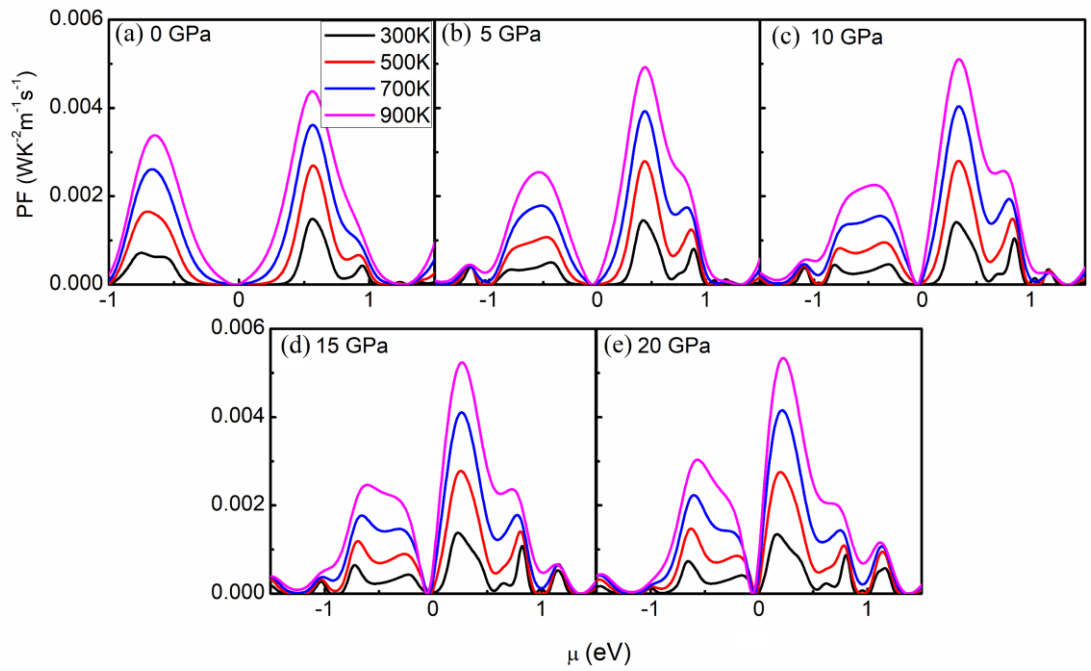


Figure 3.22. Plot of power factor (PF) for Cu_3NbTe_4 at (a) 0, (b) 5, (c) 10, (d) 15, and (e) 20 GPa pressure within CRTA.

Thermal conductivity is a measure of how easily heat flows through certain material, demonstrating that low κ_T will better maintain temperature difference, which is beneficial for TE devices that could aid in the long-term operation of such devices. As depicted in Figure 3.23, the lattice part of thermal conductivity κ_l is calculated following Equation 2.48. κ_l is found to decrease down the chalcogenide groups for each respective temperature and pressure. The maximum $\kappa_l=11.46 \text{ Wm}^{-1}\text{k}^{-1}$ being observed at 0 GPa and 300K for Cu_3NbS_4 ; and minimum κ_l as low as $1.09 \text{ Wm}^{-1}\text{k}^{-1}$ for Cu_3NbSe_4 at 10 GPa and 900K. The total thermal conductivity $\kappa_T = \kappa_l + \kappa_e$ is then obtained separately for p-type and n-type doping where κ_e is derived using the appropriate τ (RTA) as discussed in detail in the preceding section.

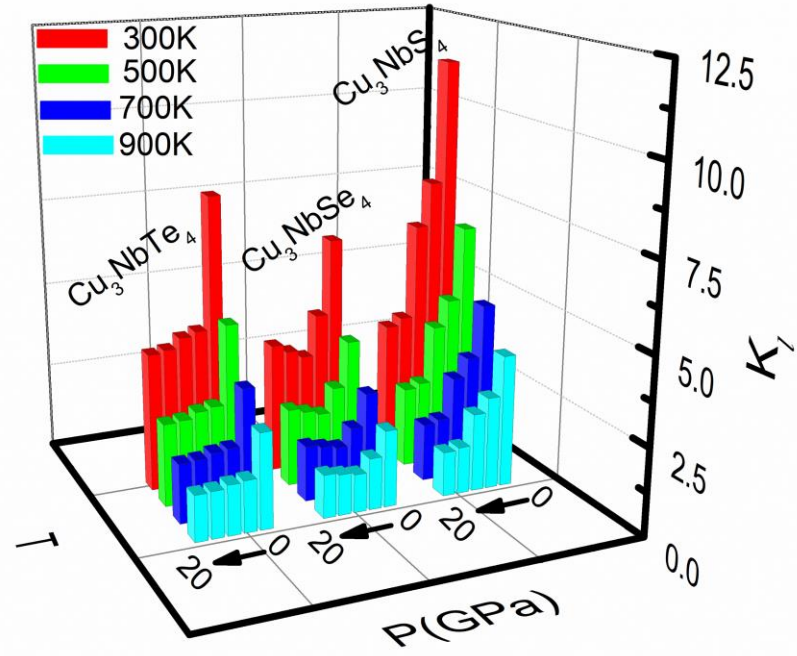


Figure 3.23. Lattice part of thermal conductivity (κ_l) in units of $\text{Wm}^{-1}\text{k}^{-1}$ for Cu_3NbX_4 ($X=\text{S, Se, Te}$) at certain temperatures and pressures obtained using Slack's equation.

The RTA using the deformation potential theory approach with effective mass approximation is implemented for transport properties study (Bardeen & Shockley, 1950; Chen et al., 2012; X. Chen et al., 2017; Fan et al., 2021; Huang & Kaviani,

2008). According to this theory, the relaxation time of charge carriers at a certain temperature can be obtained by the formula

$$\tau = \frac{2\sqrt{2}Ch^4}{3(K_B T m^*)^{3/2} E^2} \quad (3.4)$$

where C is the elastic coefficient, $\hbar$ reduced Planck's constant, K_B Boltzmann constant, T temperature, m^* effective mass, and E is deformation potential (Figure 3.24), which can further be expressed as

$$E = \frac{\Delta E_{\text{edge}}}{\Delta l/l} \quad (3.5)$$

Here, ΔE_{edge} is band edge variation (VBM or CBM) under strain in their lattice parameters (l).

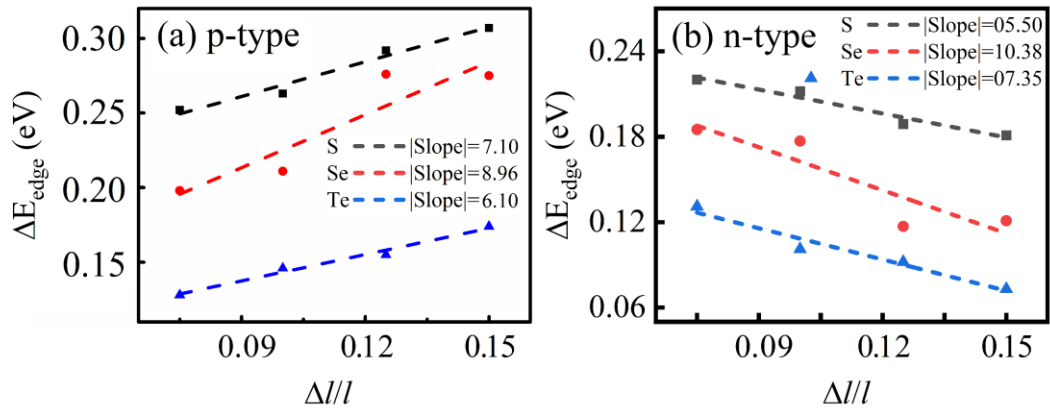


Figure 3.24. Compound dependent p-type and n-type doping deformation potential for determination of relaxation time (τ).

Effective mass plays a significant role in the prediction of materials for potential TEs. Figure 3.25 illustrates the relation of effective mass with pressure. Relatively lower or higher effective mass indicates respectively how easily or difficult charge carriers can drift due to the influence of energy. From the figure, though minute variations might occur at certain pressures, it is observed that pressure reduces the effective masses of electrons and holes in general. This suggests transport properties

enhancement concerning charge carriers. Moreover, this trend of gradual decrease in effective masses can be correlated to energy bands of Cu_3NbX_4 , where energy bands become more curved, especially in the VBM and CBM. Relaxation time τ ultimately can be obtained separately for p-type and n-type doping. Compound dependant τ is then obtained from Equation 3.4 as illustrated in Table 3.5.

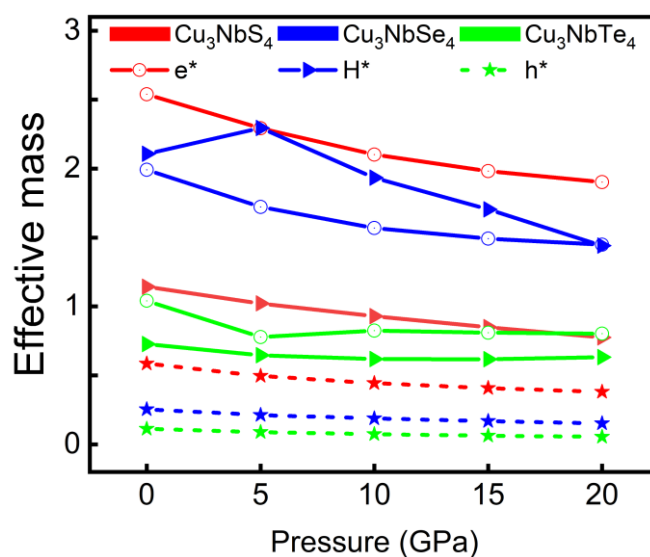


Figure 3.25. Effective mass variation with pressure for Cu_3NbX_4 with colour coding specific for each compound while e^* , H^* , and h^* is effective mass of electron, heavy hole, and light hole respectively.

Table 3.6. Calculated compound-dependant effective mass (m^*) and relaxation time (τ) $\times 10^{-14}\text{s}$ from deformation potential.

Cu_3NbX_4	Doping type	Effective mass m^*	τ (300K)	τ (500K)	τ (700K)	τ (900K)
Cu_3NbS_4	p-type	1.143	2.96	1.37	0.83	0.57
	n-type	2.540	1.49	0.69	0.42	0.29
Cu_3NbSe_4	p-type	2.106	0.63	0.29	0.18	0.12
	n-type	1.992	0.51	0.24	0.14	0.10
Cu_3NbTe_4	p-type	0.724	5.32	2.47	1.49	1.02
	n-type	1.037	2.14	0.99	0.60	0.41

The TE figure of merit ZT is perhaps the most important factor that governs the performance of TE materials. It can be illustrated that though S and σ could independently contribute towards enhancement in ZT, it should be understood that these are somewhat contradicting properties. For this reason, obtaining a reasonable ZT for practical application is quite a challenging task. Calculated ZT against temperature up to 900K is presented in Figure 3.26 by employing the formula

$$ZT = \frac{S^2 \sigma}{\kappa_T} T \quad (3.6)$$

and τ as obtained from deformation potential theory. As calculated transport properties differ by only in factors of relaxation time ' τ ', separate plots are thus not provided but rather directly implemented into the calculation of ZT. At ambient pressure, the minimum (300K) and maximum (900K) ZT are 0.14, 0.04, 0.10 and 0.40, 0.18, 0.42 respectively for X=S, Se, and Te in the p-type doping. The abnormally low ZT for Cu_3NbSe_4 , however, cannot be explained due to the diverse independent parameters. It is also noted that our results are much lower than other theoretically predicted ZT. Even at as low as 300K, Hong *et al.*, (Hong et al., 2017) predicted ZT of 0.54 and 0.48 respectively for Cu_3NbSe_4 and Cu_3NbTe_4 . Further, Enamul Haque (Haque, 2021) independently reported ZT values of 0.275, 0.485, and 0.750 at the same temperature for Cu_3NbS_4 , Cu_3NbSe_4 , and Cu_3NbTe_4 , respectively. Moreover, at 1000K both article reports $ZT > 1$ for these investigated compounds. However, when compared with experimental results from Chen, E.M. *et al.*, (E. M. Chen et al., 2017) where authors report astonishingly low ZT in the order 10^{-5} ; our calculations seem to fall closer to available experimental results. ZT values are slightly enhanced under pressure for both in the p-type and n-type doping with maximum values of 0.58, 0.26, and 0.48 for X=S, Se, and Te, respectively. Surprisingly, for Cu_3NbTe_4 , ZT is visibly reduced at 20 GPa, which is attributed to the drastic reduction in Seebeck coefficient, resulting in minimum S value.

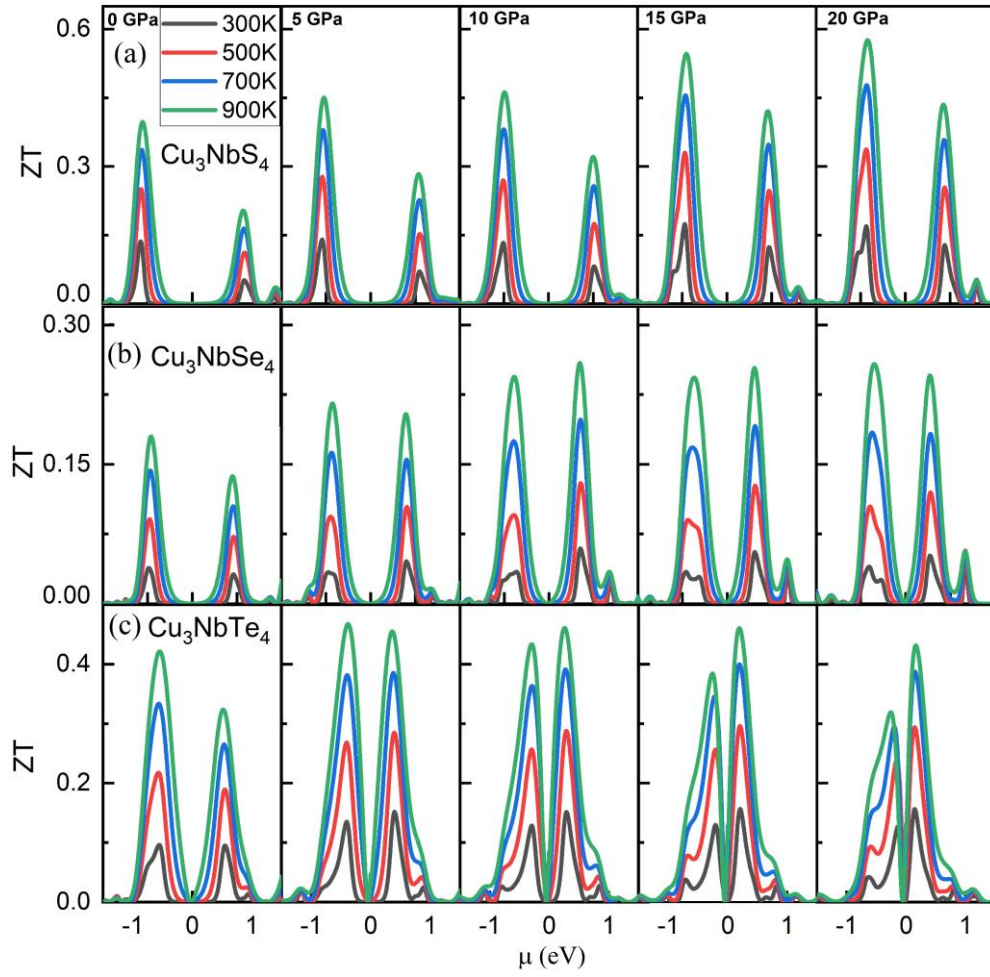


Figure 3.26. Calculated ZT using appropriate RTA for (a) Cu_3NbS_4 (b) Cu_3NbSe_4 (c) Cu_3NbTe_4 at certain temperatures for pressures of 0, 5, 10, 15, and 20 GPa.



CHAPTER 4

DOPED $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$

($x=0.00, 0.25, 0.50, 0.75, 1.00$)

PROPERTIES

4

Doped $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ ($X=0.00, 0.25, 0.50, 0.75, 1.00$) properties

This section presents the theoretical investigations of 2x2x2 supercell (SC) structure of $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ ($X=0.00, 0.25, 0.50, 0.75, 1.00$) for optoelectronic and thermoelectric applications within DFT formalism. Formation energy calculation reveals the energetical favourability of predicted compounds under doping/chemical substitution. Electronic properties are studied to understand the effect of V substitution on Nb site. The results are then correlated with optical and thermoelectric properties.

4.1 Employed parameters for $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ ($X=0.00, 0.25, 0.50, 0.75, 1.00$)

The PAW (Kresse & Joubert, 1999) potential-based *ab initio* studies into $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ have been performed using MedeA-VASP (Hohenberg & Kohn, 1964; Kohn et al., 1996; Kohn & Sham, 1965) within the GGA-PBE (Perdew et al., 1996) formalism. The already well explored bulk cubic crystal, Cu_3NbS_4 , functions as the parent compound for the substitutional doping. After full structural optimization of the bulk crystal using 8x8x8 k-mesh, 0.02 eVÅ⁻¹ ionic relaxation, and 400 eV kinetic energy cut-off, a 2x2x2 supercell is modelled, consisting of 64 atoms. Geometrical optimization was then performed in the SC with 4x4x4 k-points sampling in the Monkhorst pack scheme (Monkhorst & Pack, 1976). The decrease in k-mesh by a factor of 2 is due to an increase in real space dimensions of the supercells, subsequently decreasing in equal proportions in their reciprocal space, thus demanding lesser k-points for the same accuracy. A dense 6x6x6 k-mesh with 400 eV kinetic cut-off energy and self-consistent field (SCF) convergence of 10⁻⁵ eV was employed for electronic properties calculations. Due to semiconducting nature of the investigated compounds, the tetrahedron method with Blöchl correction was used for integration in the first Brillouin zone (Blöchl et al., 1994). A denser k-mesh of 13x13x13 was used for electron transport calculations using BoltzTraP code. The Nb atoms are then

substituted with V atoms from the pristine SC so that it takes the chemical formula $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ ($x=0.00, 0.25, 0.50, 0.75, 1.00$) wherein similar calculations for properties were then re-performed for investigation under doping/chemical substitution.

4.2 Structural and mechanical properties

The crystal structure of Cu_3NbS_4 is optimized to P-43m symmetry space groups with 5.53 Å lattice constant, which is consistent with the reported work (Chen et al., 2017; Petritis et al., 1981). Resultant SCs for various V doping levels after optimizations are shown in Figure 4.1. The calculated lattice parameter as given in Table 4.1 shows that Nb replacement does affect its structural property with a slight decrease in lattice parameter from 11.06 to 10.84 Å. The equivalent lattice constants for the same are 5.53 and 5.42 Å, respectively, which agrees well with the experimental reports of 5.50 and 5.39 Å (Van Arkel & Crevecoeur, 1963). Our theoretical results differ from experimental values by just 0.55% and 0.56%, and hence are regarded accurate for property investigation. Also, Nb replacement with V seems to preserve the cubic nature of the compounds, which agrees with the reported work on doping of S by Se (Chen et al., 2017).

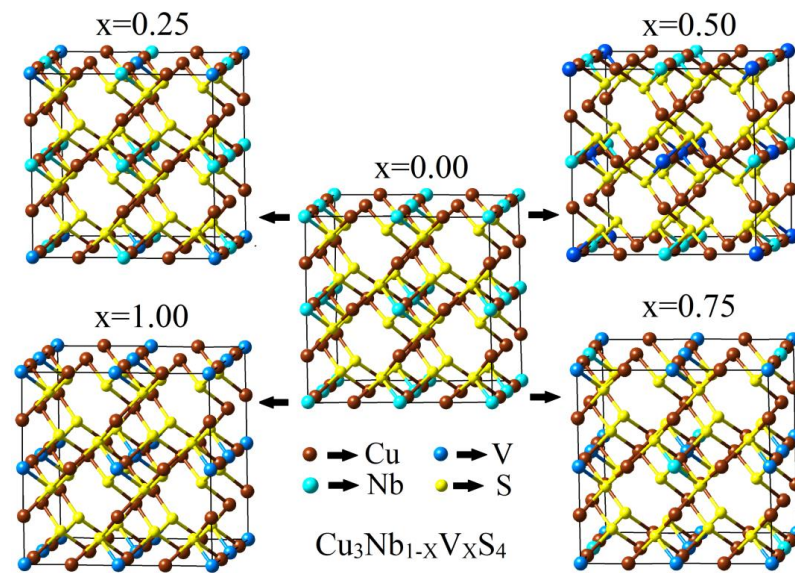


Figure 4.1. $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell illustrating various V doping levels on Nb sites.

The mechanical properties of $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell are generated according to Hill's approximation following Equation 2.33 to Equation 2.37 and is presented in Table 4.2. The SCs are found to possess greater axial resistance than shear resistance as indicated by the relatively higher magnitude of B over G. Chemical substitution doping at $X=0.25$ results in an abrupt increase in B, which eventually decreases as the doping level is raised till $X=0.75$. But when Nb-atoms are fully replaced by V-atoms, the Bulk modulus (B) slightly rises again, indicating Cu_3NbS_4 to be relatively softer than Cu_3VS_4 towards volume change. All the calculated values are below critical limits of $\nu = 0.28$ and $B/G=1.75$ for ductility, indicating non-ductility of the SC.

Table 4.1. Supercell lattice constant $a(\text{\AA})$, elastic constants C_{11} , C_{12} , C_{44} (GPa).

$\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$	a	C_{11}	C_{12}	C_{44}
X=0.00	11.06	95.40	12.40	28.32
X=0.25	11.01	102.72	20.90	29.21
X=0.50	10.96	97.92	17.44	28.06
X=0.75	10.90	95.39	15.70	25.53
X=1.00	10.84	96.25	19.25	25.01

Table 4.2. Supercell Bulk modulus B(GPa), shear modulus G(GPa), Young's modulus Y(GPa), Poisson's ratio ν , Pugh's ratio B/G, Debye temperature $\Theta(\text{K})$, and Grüneisen parameter γ .

$\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$	B	G	Y	ν	B/G	γ	Θ
X=0.00	40.07	33.02	77.71	0.18	1.21	1.20	339.1
X=0.25	48.17	33.44	81.46	0.22	1.44	1.36	346.2
X=0.50	44.27	32.43	78.19	0.21	1.36	1.31	344.2
X=0.75	42.26	30.53	73.83	0.21	1.38	1.32	326.4
X=1.00	44.92	29.75	73.10	0.23	1.51	1.40	335.3

For stability examinations, this study employs formation energy calculation, which has been widely adopted for stability predictions (Agrawal et al., 2016; Bartel et al., 2020; Liang et al., 2023; Sin et al., 2020; Tan & Ng, 2015). The calculation follows the formula (Celestine et al., 2024; Joshi et al., 2019):

$$E_{\text{form}} = \frac{1}{N} (E_{\text{total}}^i - \sum n_z E_z^{\text{bulk}}) \quad (4.1)$$

E_{form} being resultant formation energy, N the total number of atoms in the supercell, E_{total}^i the total energy of SC, n_z the total number of elements corresponding to energy E_z^{bulk} . Negative E_{form} indicates the amount of energy released for the SC formation, indicating additional relative stability for larger values while positive E_{form} will indicate relatively more instability as energy will be required for the formation of such supercells. Calculated E_{form} using Equation. 4.1 is illustrated in Table 4.3 all showing negative values, revealing their ground state energetical stabilities of the SCs.

Table 4.3. Calculated formation energy for $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell in units of eV.

$\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$	E_{total}^i	$n_{\text{Cu}}E_{\text{Cu}}^{\text{bulk}}$	$n_{\text{V}}E_{\text{V}}^{\text{bulk}}$	$n_{\text{Nb}}E_{\text{Nb}}^{\text{bulk}}$	$n_{\text{S}}E_{\text{S}}^{\text{bulk}}$	E_{form}
x=0.00	-342.90	-89.52	00.00	-40.88	-108.48	-0.99
x=0.25	-340.34	-89.52	-08.99	-30.66	-108.48	-0.98
x=0.50	-337.80	-89.52	-17.98	-20.44	-108.48	-0.98
x=0.75	-335.26	-89.52	-26.97	-10.22	-108.48	-0.98
x=1.00	-332.74	-89.52	-35.96	00.00	-108.48	-0.98

It is acknowledged that the bulk crystals of Cu_3NbS_4 , $\text{Cu}_3\text{Nb}_{0.50}\text{V}_{0.50}\text{S}_4$ and Cu_3VS_4 ($X=0, 0.5$ and 1.0) had already been synthesized experimentally (Ikeda et al., 2019). Furthermore, E_{form} remains consistent with these already synthesized compounds throughout the substitution process, implying that the SCs may likewise be stable for experimental synthesis at $X=0.25$ and 0.75 doping.

4.3 Electronic properties

Computed electronic band structures with corresponding PDOS are shown in Figure 4.2. The notable observation is the seeming transition to direct band gap nature from indirect band gap nature at the Γ -high symmetry point. This arises because as lattice dimensions in real space expand, results in an increase in number of atoms due to the $2 \times 2 \times 2$ SC. On this account, the first Brillouin zone (BZ) in reciprocal space diminishes to exactly half and more lines populate the band structure and band folding arises (Ku et al., 2010; Yang et al., 2018). This indicates that this seeming transition is perhaps due to band folding. The predicted band gaps for $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercells are 1.68, 1.29, 1.13, 1.08, and 1.03 eV for $X=0.00, 0.25, 0.50, 0.75$, and 1.00 . At $X=0.00$

and 1.00, band gaps are respectively comparable to other theoretical data of Cu_3NbS_4 and Cu_3VS_4 (Espinosa-García et al., 2017; Osorio-Guillén & Espinosa-García, 2012). From Figure 4.2(a), major contribution in the conduction band (CB) arrives from Nb-d atomic orbitals with possible minor contribution from hybridized states of S-p and Cu-d orbitals. Further, in the valence band (VB) minor equivalent contribution near the Fermi level ($E_F=0$ eV) is observed from all possible hybridized states of S-p, V-d, and Cu-d orbitals while Cu-d has a major influence in the deeper energies (-1.2 eV) leading to the unique electronic band profile.

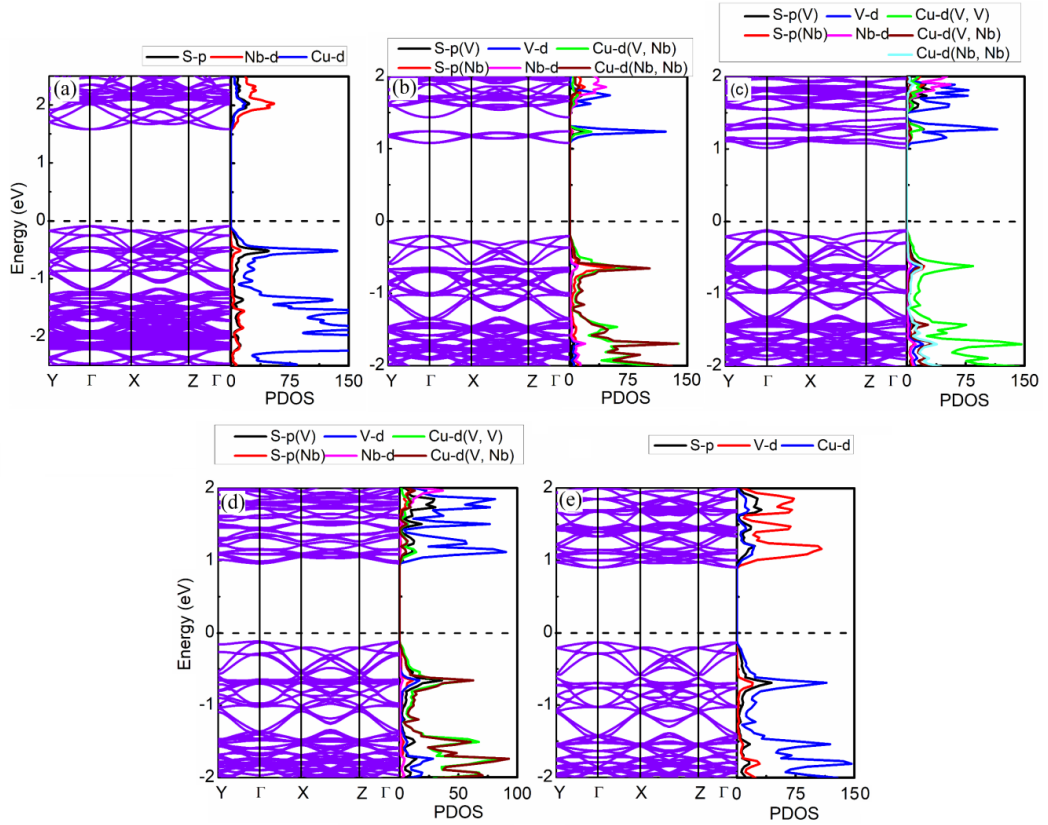


Figure 4.2. Band structure with corresponding PDOS (states/eV) of $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$. (a) $x=0.00$, (b) $x=0.25$, (c) $x=0.50$, (d) $x=0.75$, and (e) $x=1.00$. Here, S-p(Z) corresponds to S atoms bonded to Z atoms, Cu-d(A, B) corresponds to Cu atoms sandwiched between A and B atoms in the SCs.

The PDOS contributions from different atomic valence orbitals are further

divided as illustrated in the figure description, according to bonding pairs and atomic positions in the SC, etc. In the presence of Nb and V atoms, it is perceptible that contributions near the E_F by Nb atoms are suppressed, which is evident from higher V concentration (Figure 4.2(c) and Figure 4.2(d)). Doping at $X=0.25$ results in the formation of isolated and unique energy bands that constitute the CB edge. Formation of the depleted energy band-like gap is observed around 1.3 eV, which is revealed by the devoid of PDOS. These bands lead to the sudden decrease in band gap by an astonishing 0.39 eV, resulting in the highest band gap shift due to substitution. The corresponding set of PDOS peaks is mainly revealed by blue, green, and black colour curves, each representing V-d, Cu-d(V, Nb), and S-p(V) orbital contribution, respectively. It is evident that V-atom has a great influence on the existence of this PDOS peak while Nb primarily contributes only to higher energy bands in the CB; thus, the decrease in band gaps with V substitution on Nb sites. Surprisingly, the same atomic orbitals exhibit different magnitudes of PDOS according to their bonding and atomic positions, etc. In a general sense, a relatively higher PDOS could signify a higher contribution by that particular atom (orbitals) in the formation of that respective compound and vice versa. Accordingly, V has higher PDOS than Nb, signifying greater orbital contribution towards the compound formation. This could be due to the higher electronegativity of V than Nb from Pauling's electronegativity scale implying relatively higher reactivity for V. Perhaps for this same reason, the PDOS contributions from Cu-d(V, Nb) and S-p(V) are thus higher than Cu-d(Nb, Nb) and S-p(Nb) respectively. Following this trend, especially in the CB, we can anticipate that atoms in and around having maximum number of V atoms will have maximum PDOS contribution in the energy band profile. The electronic band structures with PDOS at $X=0.50$ V are shown in Figure 4.2(c). In this doping level, equal number of V and Nb atoms (4 each) are present in the SC with a visible diminishing band gap due to shifting of band edge towards the E_F from CB. Also, distinct discontinuity of bands continues to occur around the same energy where depletion in PDOS was previously observed. Though diverse atomic orbitals contribute to these peculiar isolated bands in the CB, negligible contribution arrives from Nb atomic orbital states. Distinct PDOS for Cu-d(V,V), Cu-d(V, Nb), and Cu-d(Nb, Nb) are also observed with varying magnitudes, as expected. When replacement by V is increased to 0.75, previously observed isolated

energy bands become almost continuous with the higher energy bands with slight decrease in band gap. As expected, V contribution now becomes overwhelmingly large both in the VB as well as CB as compared to Nb. All these findings led to the understanding of sudden drop followed by the gradual decrease of energy band gap in the investigated SC from 1.29 eV at X=0.25 to 1.03 eV at X=1.00.

4.4 Optical properties

Resultant optical properties of the complex dielectric constants, complex refractive index, absorption coefficient, and theoretical optical band gap $E^{\text{opt}}(\text{DFT})$ as a function of photon energy for $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell as illustrated in Figure 4.3 to Figure 4.5. The first to be investigated is perhaps the dielectric function, which consists of real part ϵ_1 and imaginary part ϵ_2 . It is also from this function that all other optical properties can be subsequently derived. The complex function can be expressed in the following Equation 2.39 and Equation 2.40 (Ambrosch-Draxl & Sofo, 2006):

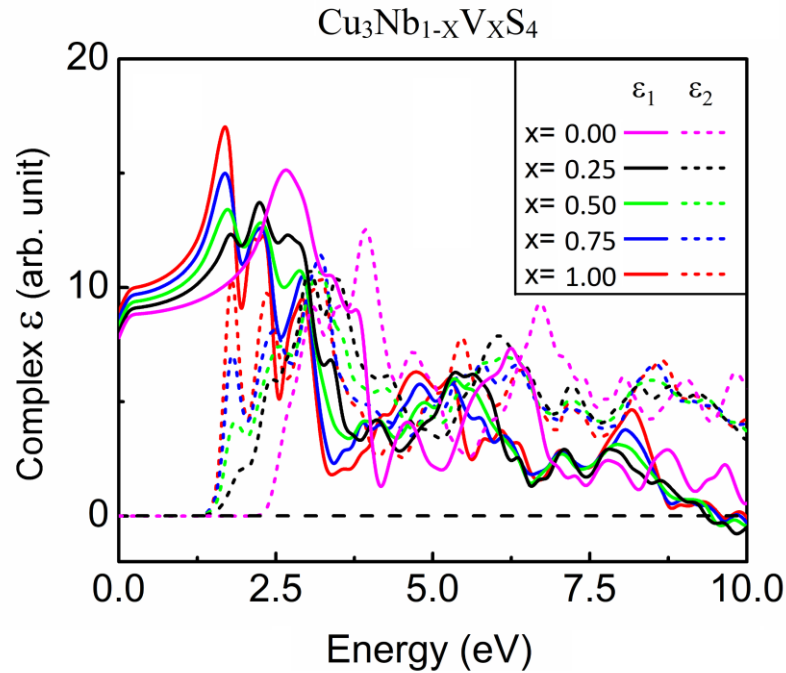


Figure 4.3. Predicted complex dielectric function (ϵ) in arbitrary units for $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ demonstrating red shifting in optical activity with doping concentration for enhanced optical properties.

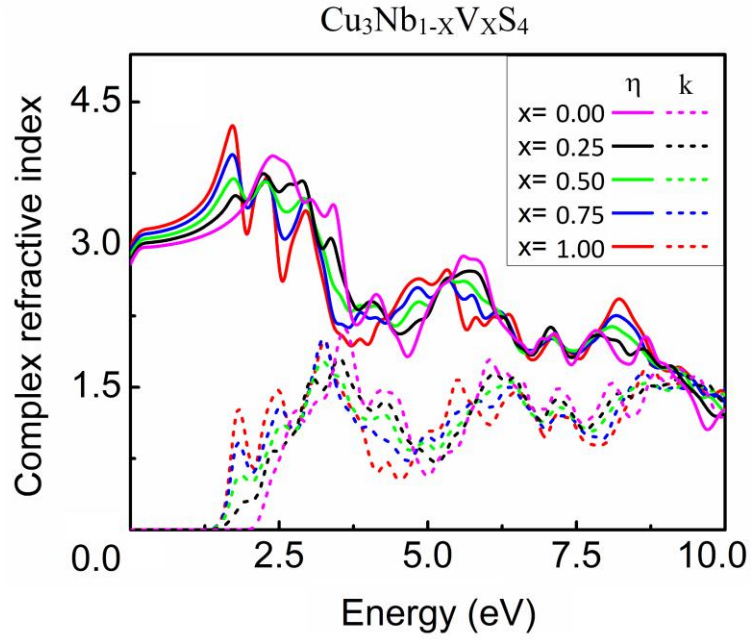


Figure 4.4. Deduced extinction coefficient (k) and refractive index (η) for $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$.

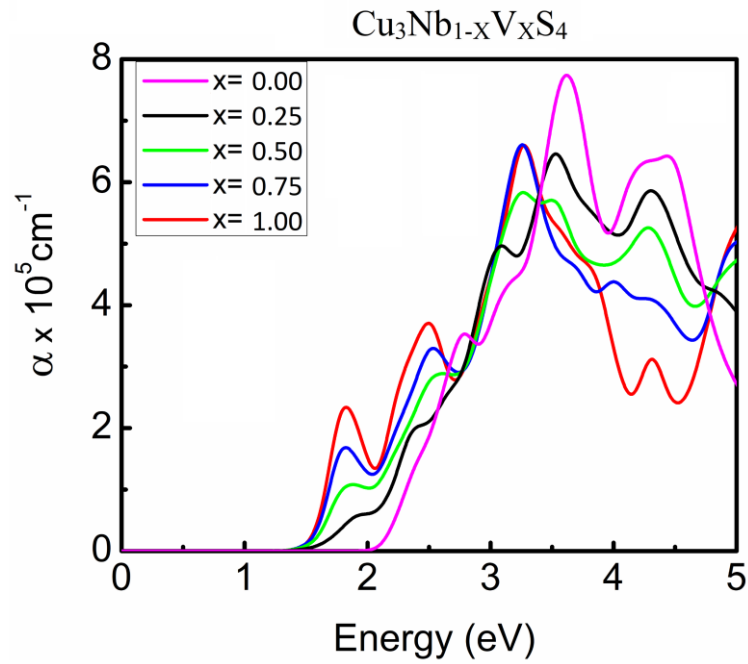


Figure 4.5. Deduced absorption coefficient (α) $\times 10^5 \text{ cm}^{-1}$ for $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ demonstrating enhanced optical absorption coefficient and red shifting with doping concentration.

The complex dielectric function plot for various levels of substitution is illustrated in Figure 4.2(a). The real part of dielectric function ϵ_1 typically measures the polarization of certain materials due to incident radiation. The static dielectric constant is determined when no photon falls on the material, i.e. $\epsilon_1(0)$ and are calculated to be 7.86, 8.22, 8.46, 8.70, and 9.05 arb. unit respectively for $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ ($x=0.00, 0.25, 0.50, 0.75$, and 1.00). ϵ_1 is closely related to the refractive index η as shown in Figure 4.2(b). The η also provides us with additional information on anomalous dispersion, which is of importance, especially in the visible energy range for potential PV applications. Anomalous dispersion will occur in regions where η decreases with increase in photon energy. This is a significant notable consequence as this often arises in regions of strong optical absorption. Initially, η peaks drastically red shifts at $x=0.25$, which gradually decreases with increase in x . This ultimately could indicate strong optical absorption in the lower photon energies. Characteristic trend is followed by $\epsilon_1(\omega)$ and hence by η for certain Nb replacement except at $x=0.00$, where there exists a unique drastic change in the plot due to the absence of V atoms.

The interband transitions can be mostly defined from the imaginary part of the dielectric function ϵ_2 , which is closely related to extinction coefficient k that further correlates to absorption coefficient α employing Equation 2.43. The ϵ_2 and perhaps k remains zero for certain specific photon energy after which continuous optical activity persists within the studied energy range. At $x=0.00$ and 0.25 , the electronic band profile and thus, resultant optical properties vary significantly. Minute optical activity exists for $\text{Cu}_3\text{Nb}_{0.75}\text{V}_{0.25}\text{S}_4$ at ~ 1.82 eV due to interband transition between the unique PDOS peaks in the CB and S-p, Cu-d states in the VB. This optical activity for a particular photon energy of ~ 1.82 eV vanishes for $x=0.00$ as it falls well below the $E^{\text{opt}}(\text{DFT})$ (see Figure 4.3 to Figure 4.5). Moreover, stronger optical activity exists in higher photon energy for Cu_3NbS_4 and $\text{Cu}_3\text{V}_{0.25}\text{Nb}_{0.75}\text{S}_4$ supercell due to the participation of deeper/higher energy bands from both CB and VB. In higher concentrations of $x=0.50, 0.75$, and 1.00 , first optical peaks are observed at ~ 1.82 eV, which corresponds to the interband transition between Cu-d and V-d states in general. Furthermore, the second optical peaks are observed at ~ 2.42 eV after a dip in

magnitude, which corresponds to transition between the same states but from higher energies in the CB. This can be understood due to the presence of multiple PDOS peaks which provide additional states for direct transitions. The $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell exhibits a good absorption coefficient α in the order of 10^5 cm^{-1} at all levels of V-substitution as shown in Figure 4.5. With regards to prospects for optoelectronics, our investigated SC with thickness 100 nm could strongly absorb photons, paving the path for potential PV for certain V-substitution in the visible region. The onset of α is utilized for predicting $E^{\text{opt}}(\text{DFT}) = 2.11, 1.64, 1.56, 1.53,$ and 1.53 eV respectively, for $X=0.00, 0.25, 0.50, 0.75,$ and 1.00 . Our predicted values are quite comparable to experimental optical band gaps $E^{\text{opt}}(\text{Expt.})$ reported by Ikeda S *et al.*, (Ikeda et al., 2019) where band gaps are obtained from their absorption edge, which is analogous to our theoretical approach in predicting $E^{\text{opt}}(\text{DFT})$. The $E^{\text{opt}}(\text{DFT})$ consistency at $X=0.75$ and 1.00 can be realized from their comparable electronic band structures. A pictorial representation of band gap variation with certain V concentrations is illustrated in Figure 4.6 for easier comparison.

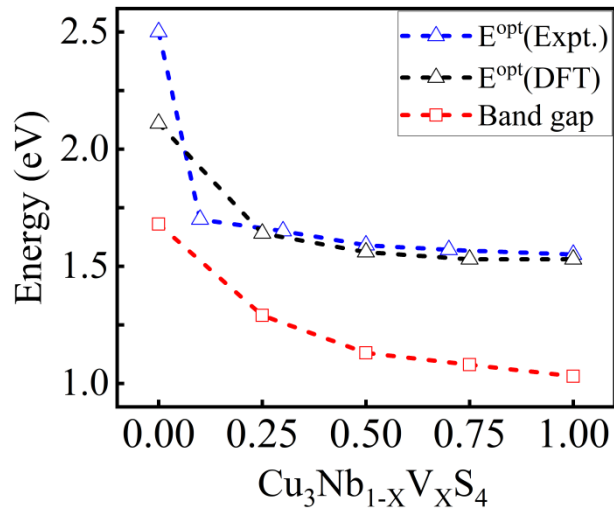


Figure 4.6. Variation of experimental $E^{\text{opt}}(\text{Expt.})$, $E^{\text{opt}}(\text{DFT})$, and fundamental energy band gaps (eV) in $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$.

4.5 Thermoelectric properties

Transport properties for prediction of TE properties are carried out following the semi-classical Boltzmann transport theory. This theory suggests that electrons follow classical equations of motion between scattering events separated by relaxation time, while depending on the quantum-mechanical calculation of the electronic states. Within the default constant relaxation time approximation (CRTA) of $\tau=10^{-14}$ s as implemented in the BoltzTraP code, we present the electron transport coefficients such as the Seebeck coefficient (S), electrical conductivity (σ), the total thermal conductivity (κ_T) which is derived from the electronic part (κ_e) and the lattice part (κ_l) of thermal conductivity, the TE power factor (PF), and finally, the dimensionless TE figure of merit (ZT). For this study, we find CRTA as an advantage of the computational method since it enables more clearly the factors that generate modifications in attainable power factor for different levels of chemical substitution [60]. The melting point of Cu_3NbS_4 is experimentally measured to be $\sim 1100\text{K}$, and thus we truncate our calculations at this temperature (Chen et al., 2017).

Calculated S for various temperatures with respect to -1.5 eV to 1.5 eV chemical potential range for the investigated SCs are shown in Figure 4.7. The negative chemical potential illustrates p-type doping properties while n-type doping properties by positive chemical potentials. It is observed that $|S|$ is maximum at the lowest temperature. i.e., 300K and decreases with increasing temperature attaining the lowest at 1100K within a particular plot. Moreover, at a particular given temperature, we observe a decrease in $|S|$ with V concentration, attaining its maximum $2745\text{ }\mu\text{VK}^{-1}$ for Cu_3NbS_4 supercell. The diminishing $|S|$ with V substitution can be explained by the corresponding reduction of band gaps, which led to an increase in carrier concentration of thermally excited charge carriers.

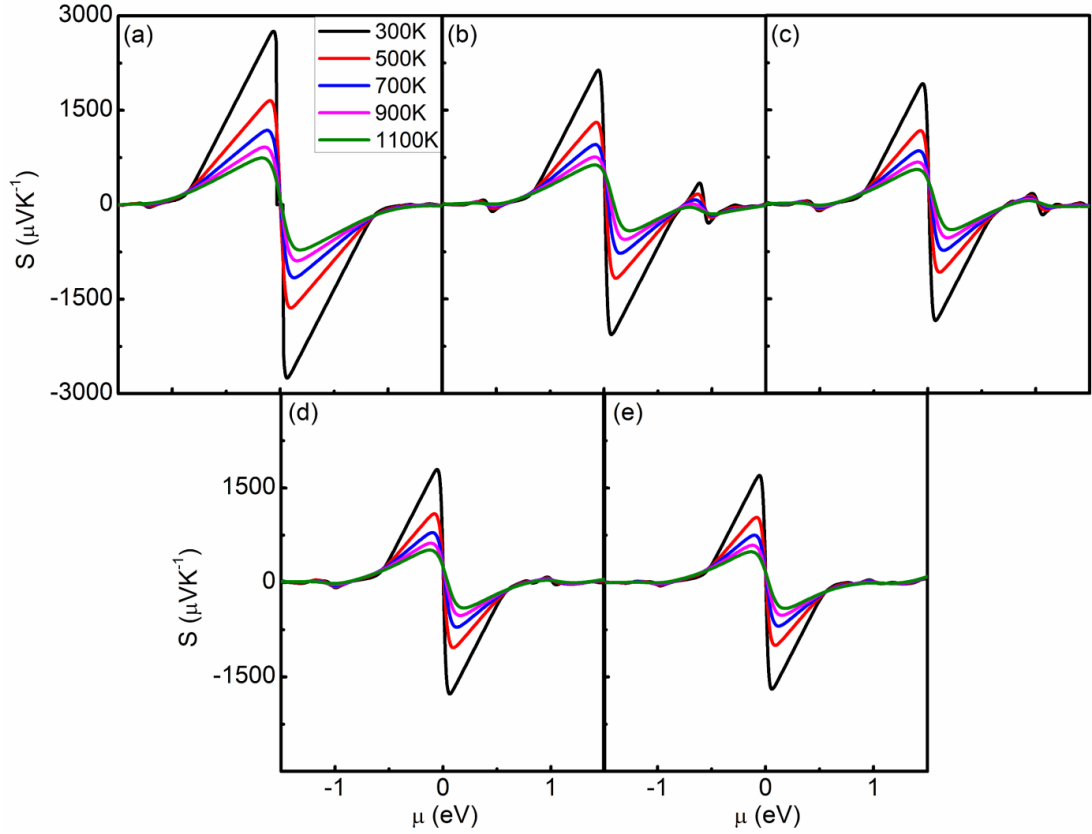


Figure 4.7. Calculated Seebeck coefficient for $\text{Cu}_3\text{Nb}_{1-X}\text{V}_X\text{S}_4$ supercell: (a) $X=0.00$ (b) $X=0.25$ (c) $X=0.50$ (d) $X=0.75$ (e) $X=1.00$.

The resultant electrical conductivity σ obtained from Equation 2.45 is shown in Figure 4.8 (a-e). Our investigated SC possesses favourable σ in the order of 10^5 Sm^{-1} . The conductivity first decreases for $\text{Cu}_3\text{Nb}_{0.75}\text{V}_{0.25}\text{S}_4$ as compared to Cu_3NbS_4 supercell and then gradually increases for higher X values. Though many factors could contribute to this phenomenon, one of the straightforward reasons could be the diminishing band gaps. With reduced band gaps, charge carriers require lesser amount of energy to thermally excite and resulting in interband transitions, effectively enhancing σ . However, a typical decline in $\text{Cu}_3\text{Nb}_{0.75}\text{V}_{0.25}\text{S}_4$ supercell could be due to a relative decrease in the population of charge carriers in the VB near E_F , as revealed from PDOS (see Figure 4.2(b)).

Using the values calculated for $|S|$ and σ , the effective TE power factor (PF) is obtained using Equation 2.47. The power factor PF is found to be in the moderate

range, highest for Cu_3VS_4 supercell with a decrease in magnitude under certain V/Nb concentration, then rises again in Cu_3NbS_4 supercell. This trend of decreasing and increasing in PF can be understood from the nature of $|S|$ and σ as discussed earlier. Also, within a particular supercell, p-type doping is relatively higher than its n-type doping counterpart, indicating p-type semiconducting nature of the SC.

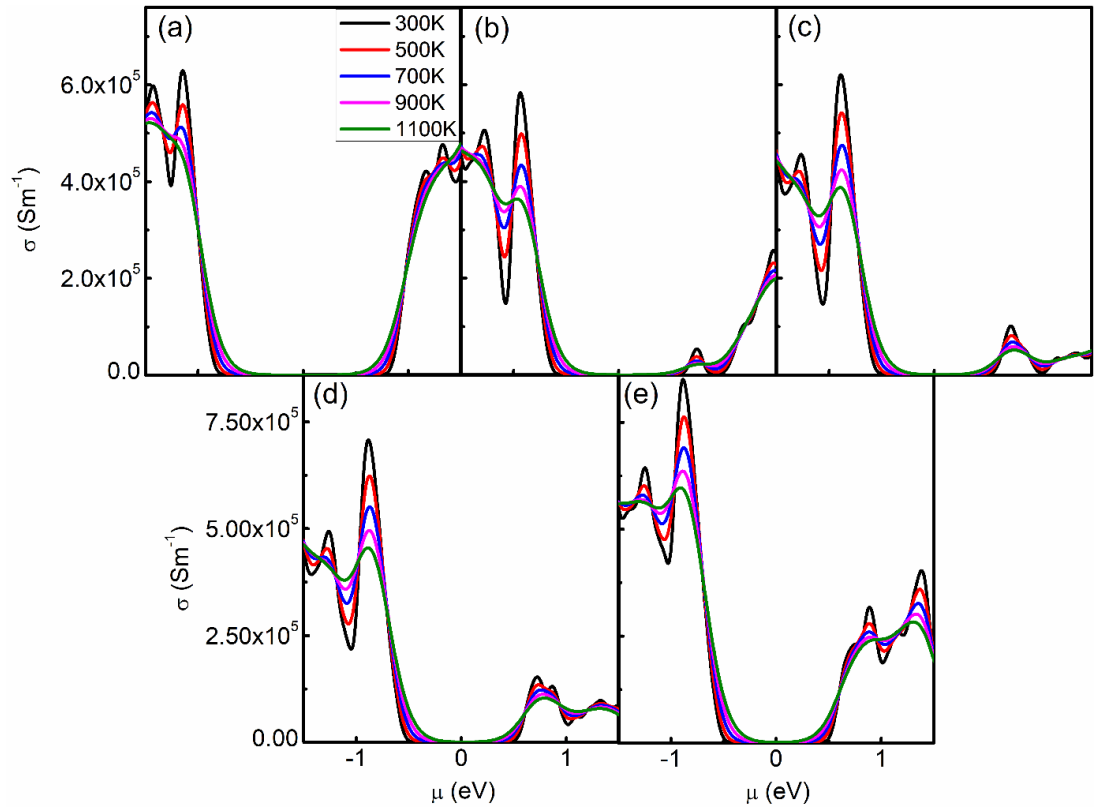


Figure 4.8. Calculated electrical conductivity for $\text{Cu}_3\text{Nb}_{1-X}\text{V}_X\text{S}_4$: (a) $X=0.00$ (b) $X=0.25$ (c) $X=0.50$ (d) $X=0.75$ (e) $X=1.00$.

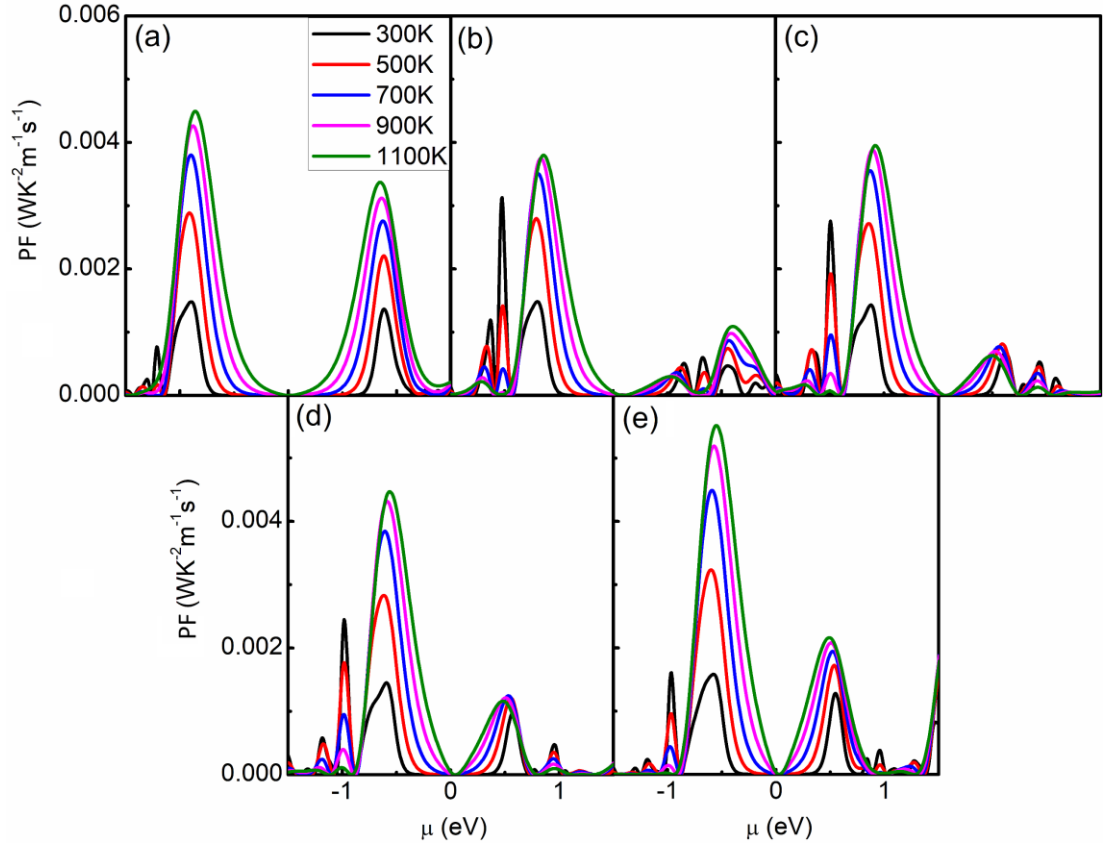


Figure 4.9. Resultant power factor (PF) of $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell: (a) $X=0.00$, (b) $X=0.25$, (c) $X=0.50$, (d) $X=0.75$, (e) $X=1.00$.

Even materials with high PF can still be rendered ineffective for TE if they possess high thermal conductivity. As previously discussed, thermal conductivity constitutes the lattice part of thermal conductivity κ_l and the electronic part of thermal conductivity κ_e as seen from Equation 2.46 and Equation 2.48.

The electronic part of thermal conductivity κ_e can be regarded as the thermal contributions due to the movement of charge carriers and is closely related to σ . A more definite understanding can be drawn from κ_e plot rather than σ as its variation with temperature becomes more distinct as shown in Figure 4.10. This indicates the direct proportionality of κ_e with temperature as predicted. Several methods have been approached for the calculations of κ_l . Some reports employ computationally demanding calculations like ShengBTE (Li et al., 2014) and first-principles Debye-Callaway (Zhang, 2016) approach, and there are others using high-throughput

materials modelling especially for half-Heusler compounds (Carrete et al., 2014). Further, Qin *et al.*, (Qin et al., 2022) asserts to have optimised the A parameter from Slack's equation, which could predict overall more accurate κ_l . Thus, for this current study, we employ the semi empirical Slack's equation with the optimised A parameter according to Qin *et al.*, (Qin et al., 2022), since it is the most widely used for low end computational devices due to the impracticality of obtaining results from the seemingly more accurate but computationally demanding calculations. The optimised constant A is obtained from γ using the formula:

$$A = \frac{1}{1 + \frac{1}{\gamma} + \frac{8.3 \times 10^5}{\gamma^{2.4}}} \quad (4.2)$$

The calculated κ_l obtained from Equation 2.48 utilizing the optimized A is shown in Figure 4.11. The apparent difference of κ_l from κ_e is its inverse proportionality with temperature. Though phonon vibrations should increase with temperature, which would lead to a net increase in thermal conductivity, the contrary occurs due to Umklapp scattering, increasing the thermal resistance and leading to a net decrease in κ_l . Further, κ_l can be correlated with sound velocities using Equation 2.36. Predicted u_m for X=0.00, 0.25, 0.50, 0.75, and 1.00 are 3151, 3201, 3167, 2989, and 3055 ms^{-1} respectively. As such, κ_l also correspondingly increase or decrease with sound velocities for various doping levels.

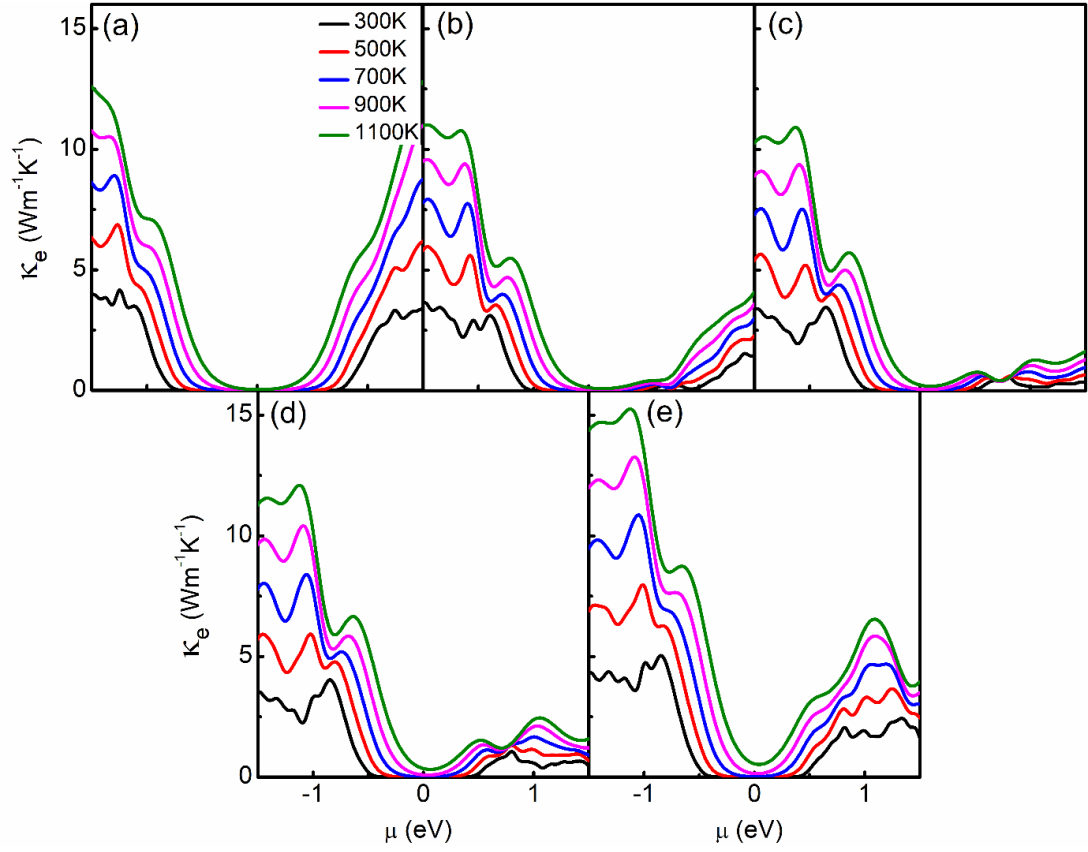


Figure 4.10. Calculated electronic part of thermal conductivity for $\text{Cu}_3\text{Nb}_{1-X}\text{V}_X\text{S}_4$ supercell: (a) $X=0.00$ (b) $X=0.25$ (c) $X=0.50$ (d) $X=0.75$ (e) $X=1.00$.

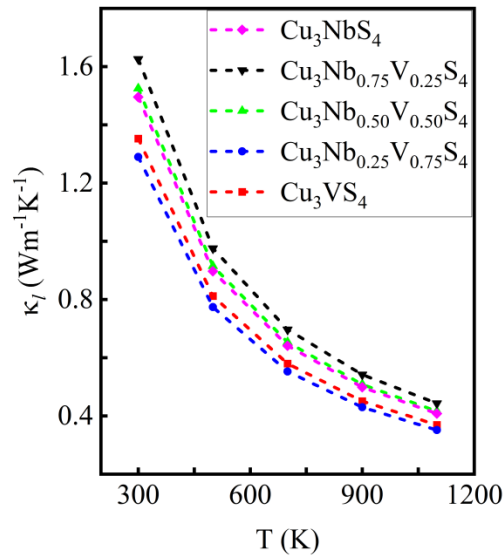


Figure 4.11. Predicted lattice part of thermal conductivity for $\text{Cu}_3\text{Nb}_{1-X}\text{V}_X\text{S}_4$ supercell.

Figure 4.12 illustrates the dimensionless TE efficiency figure of merit ZT for p-type and n-type doping utilizing S , σ , κ_T , and T parameters using the formula

$$ZT = \frac{S^2 \sigma}{\kappa_T} T \quad (4.3)$$

The SCs exhibit promising TE properties as observed from the figure. P-type doping exhibits higher ZT for a specific temperature than its n-type doping counterpart. At 1100K, p-type doping reveals moderate ZT around 0.80 at all X concentrations, indicating almost an independence on doping levels, whereas n-type doping exhibits diverse ZT exhibiting low values in some cases. P-type doping at all X concentrations demonstrates potential TE device application with maximum $ZT=0.83$ for both $\text{Cu}_3\text{Nb}_{0.25}\text{V}_{0.75}\text{S}_4$ and Cu_3VS_4 at 1100K. Though Figure 4.9 demonstrates low PF for n-type doping, the unexpectedly comparable ZT with p-type doping, especially at $X=0.00$ and 1.00 , is due to volatile deviations in κ_e resulting in the unique ZT values.

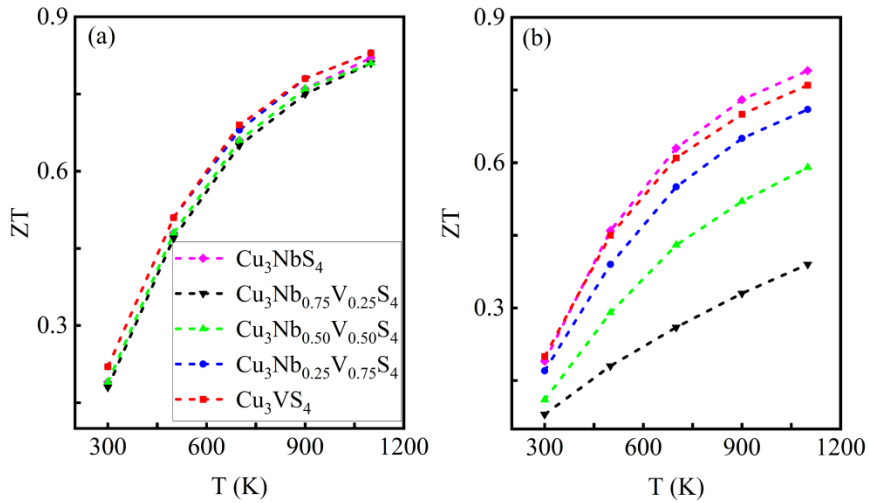


Figure 4.12. Predicted maximum ZT for $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell to temperature for: (a) p-type and (b) n-type doping.

CHAPTER 5

AB INITIO THIN FILM PROPERTIES

OF

Cu_3TaTe_4 (100) SURFACE

5

***Ab initio* thin film properties of Cu_3TaTe_4 (100) surface**

Despite various experimental studies with promising results as pointed out in Chapter 1, to the best of our knowledge, there is no theoretical study on the surface properties of CSC thin films till today. However, surface properties have been reported to play a vital role in determining the properties of thin films as a whole (Eglitis, 2015; Guan et al., 2009; Ondráček et al., 2012; Sholl & Steckel, 2009; Sun & Ceder, 2013; Tian et al., 2018; Zeng et al., 2022). So, in this chapter, we investigate Cu_3TaTe_4 (100) surface properties by modelling a free-standing slab along the z-axis from the optimized Cu_3TaTe_4 bulk structure. To make our study systematic, we consider only symmetric terminations with CuCu, CuTa, TeTe(1), and TeTe(2) atoms at the surface. The bulk and surface electronic properties are then analysed and compared. Further, surface energy of each termination is calculated to examine their stabilities for possible practical fabrication. Lastly, a more thorough investigation is conducted to verify assertions on the anticipated possibility of surface reconstruction in TeTe(2) surface terminal.

5.1 Employed parameters for Cu_3TaTe_4 (100) surface

The first-principles calculations were carried out using spin-polarized DFT (Hohenberg & Kohn, 1964; Kohn & Sham, 1965), based on the PAW (Blöchl, 1994; Kresse & Furthmüller, 1996a, 1996b; Kresse & Joubert, 1999) approach as implemented and programmed in MedeA-VASP. The exchange-correlation energy within the GGA-PBE (Perdew et al., 1997) formalism is used to treat all electron interactions. For the bulk and (100) surface, plane wave kinetic energy cutoff was set to 400 eV. The self-consistent field calculation steps were carried out until the energy difference is less than 10^{-5} eV. To study the stability and electronic properties of Cu_3TaTe_4 (100) surface, surface slab models having 13/15 atomic layers with four

different symmetrical terminations CuCu, CuTa, TeTe(1) and TeTe(2) along (100) plane have been built. Structural optimizations were accomplished with the conjugate gradient technique with a force tolerance of 0.01 eV/Å. The explicit k-mesh chosen for bulk and surface calculations are 8 x 8 x 8 and 10 x 10 x 1 Monkhorst pack grid (Monkhorst & Pack, 1976) respectively. For electronic properties calculation, an even denser k-mesh of 12 x 12 x 1 is sampled to integrate the first Brillouin Zone.

5.2 Bulk Cu₃TaTe₄

The conventional cubic crystal structure is specifically chosen for M=Ta and X=Te such that the crystal takes the chemical formula of Cu₃TaTe₄ as shown in Figure 1.2. After optimization, the lattice parameter is 6.007 Å, which has a relative error of about ±1.30% only as compared to values from experiment (J. Li et al., 1995). A slight overestimation of our calculated lattice constant is typical for GGA approach (Haas et al., 2009). Good agreement in the calculated lattice parameter with experimental value validates the consistency of our bulk structure calculations and its suitability for further surface investigation.

Before proceeding to surface properties, the electronic properties of the bulk crystal are first calculated and presented in Figure 5.1. The electronic band structure shows indirect band gap semiconducting nature with conduction band minima (CBM) and valence band maxima (VBM) located at the X and R high symmetry points respectively. The energy band gap value obtained 1.16 eV is consistent with reported results obtained using DFT calculations with GGA-PBE functional (Ali et al., 2016). Further, DOS of the bulk structure shows symmetry around the Fermi Energy (E_F) for both spin up and spin down channel, thus revealing the nonmagnetic nature of the compound with net zero spin polarization. The PDOS plot shows that the energy states near the conduction band edge mainly originate from Ta-d orbitals, while the corresponding energy states in the valence band (VB) are mainly due to hybridization of Cu-d and Te-p.

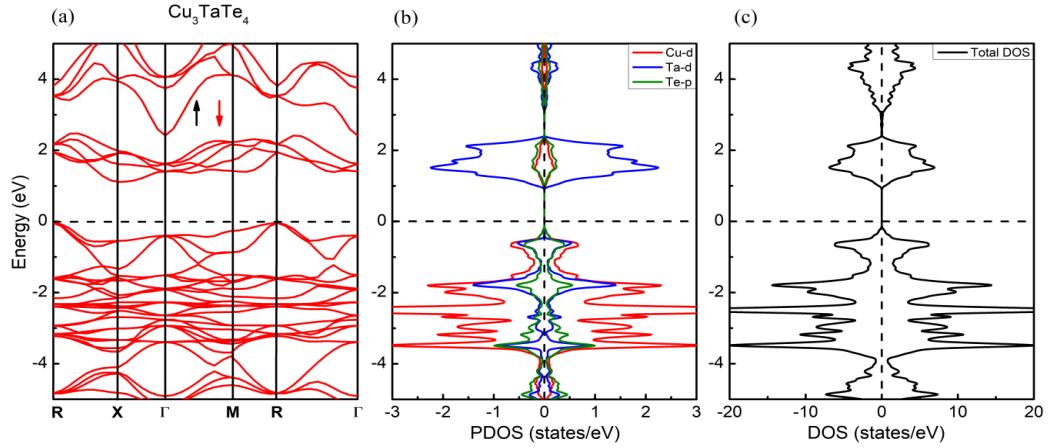


Figure 5.1. Bulk Cu_3TaTe_4 (a) electronic band structure (b) PDOS (c) Total DOS exhibiting the same nature for spin-up and spin down channel, demonstrating non-magnetic nature of the bulk compound.

5.3 Surface and structural relaxation

The theoretical DFT surface slab model approach has been discussed in detail in section 1.4 of Chapter 1. Conventional (100) symmetric surface slab models of Cu_3TaTe_4 considered for this work are shown in Figure 5.2. This is done to eliminate any unfavourable induced polarization caused by unsymmetrical surface terminations (Sholl & Steckel, 2009). To achieve symmetric terminations, the surfaces are cleaved at different thicknesses depending on the terminations chosen. This results in different number of atomic layers. While there are only 13 atomic layers for both CuCu and CuTa surface terminations, there are 15 atomic layers for both TeTe(1) and TeTe(2) surface terminations. To avoid interactions from the neighbouring periodic repetitions along the z axis, a vacuum of 15 Å (Sun & Ceder, 2013) is applied on both the top and bottom surfaces. When performing structural optimization, only the first four outer atomic layers on either side of the surfaces are relaxed (Y. S. Li et al., 1989; Sun & Ceder, 2013) while the remaining inner atomic layers, i.e., 5 central layers for CuCu and CuTa surface terminations and 7 central layers for TeTe(1) and TeTe(2) surface terminations are considered as core region and atoms are fixed such that they resemble their bulk positions. This approach is followed to achieve optimization without significant loss to accuracy.

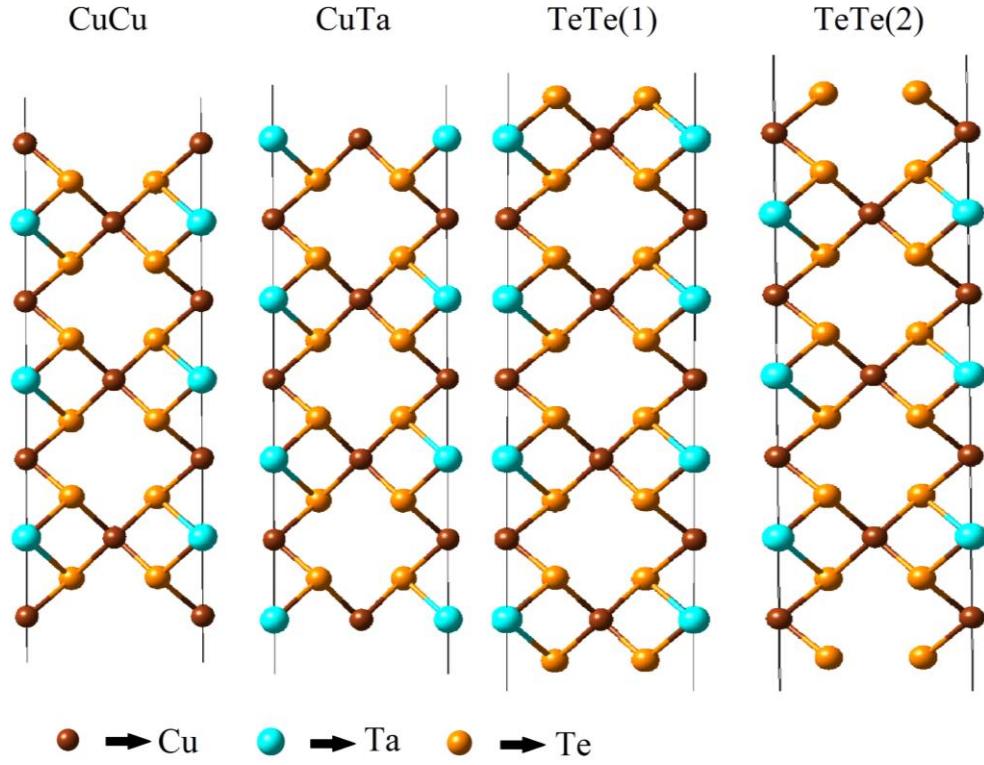


Figure 5.2. Conventional free standing surface slab models of $\text{Cu}_3\text{TaTe}_4(100)$ surface for all four possible symmetric terminations. Nomenclature of the surface slabs so selected according to their specific terminations.

Structural parameters after relaxation are given in Table 5.1. When considering surface atoms, reduction of coordination numbers occurred due to the breaking of translational symmetry. This usually results in either contraction or expansion of interatomic distances to minimise energy. In Table 5.1, ‘d’ denotes distance between adjacent atomic layers shown in Figure 5.3. Atomic layers of surface slab models are identified with the Greek letter σ . Here, σ represents the outermost atomic layer, which is the atoms at the surface. $\sigma-1$ represents the immediate subsurface atomic layer just beneath the surface. $\sigma-2$ and $\sigma-3$ represent the deeper subsequent subsurface atomic layers. The subscripts i and f in the table denote initial and final positions after relaxation respectively. Thus, $\Delta d_{f-i} = d_f - d_i$ represents the changes in interatomic distances between atomic layers after relaxation. Positive value of Δd_{f-i} represents expansion and negative value of Δd_{f-i} represents contraction. The percentage changes

in the table are calculated with respect to the bulk lattice parameter. Except for the TeTe(2) termination, it is observed that all the three other terminations exhibit compression of the distance between atomic layer at the surface and the adjacent subsurface. However, the extent of compression varies from one termination to another with 6.16%, 3.44%, and 0.20% for CuCu, CuTa and TeTe(1) surface terminations respectively. This inward relaxation of the outermost surface indicates potential of the slab to hold the outermost atomic layer, which is an important criterion for stability of a surface. In addition, the three surface terminations follow the same trend of alternatingly decreasing and increasing inter-layer separation after relaxation when moving deeper into the subsequent atomic layers. As for the TeTe(2) termination, the distance between the outermost atomic layer and the immediate subsurface atomic layer expands drastically by an astonishing amount of 13.01%. This outward relaxation could be attributed to the metallicity of the surface, which could result in the surface atomic layers attempting to reorganise the displaced valence electron density (Chis & Hellsing, 2004). Apart from this, the two subsurface atomic layers (σ -1, σ -2) experience contraction by 1.96% and 0.15% respectively, while σ -3 surface expands by 0.19%.

Table 5.1. The four surface terminations of Cu₃TaTe₄(100) with calculated slab thickness, layer under consideration, initial d_i and final d_f, change in d after relaxation Δd_{f-i} and percentage change with respect to bulk lattice constant (all distance in units of Å).

Terminal	Slab thickness	Layer	d _i	d _f	Δd _{f-i}	% of Δd _{f-i}
CuCu	17.4	CuCu σ	1.464	1.094	-0.370	-6.16
		TeTe σ-1	1.540	1.613	0.073	1.22
		CuTa σ-2	1.540	1.514	-0.026	-0.42
		TeTe σ-3	1.464	1.489	0.025	0.42
CuTa	17.4	CuTa σ	1.540	1.333	-0.207	-3.44
		TeTe σ-1	1.464	1.534	0.070	1.17
		CuCu σ-2	1.464	1.445	-0.018	-0.31
		TeTe σ-3	1.540	1.554	0.014	0.23
TeTe(1)	21.2	TeTe σ	1.540	1.528	-0.012	-0.20
		CuTa σ-1	1.540	1.570	0.030	0.49
		TeTe σ -2	1.464	1.440	-0.023	-0.39
		CuCu σ -3	1.464	1.476	0.012	0.20
TeTe(2)	22.3	TeTe σ	1.464	2.245	0.782	13.01
		CuCu σ -1	1.464	1.346	-0.118	-1.96
		TeTe σ -2	1.540	1.531	-0.009	-0.15
		CuTa σ -3	1.540	1.551	0.011	0.19

5.4 Surface stability

The energetical stability of each of the four surface slab models having different terminations are estimated by calculating the surface energy. This will provide necessary theoretical data for practical realization of thin films with different surface terminations along (100) plane. The surface energy consists of two terms, such as the relaxation energy and the cleavage energy. The relaxation energy (E_r), which is the amount of energy required to relax both sides of the surfaces is expressed as (Takagi et al., 2016; Tian et al., 2018; Tran et al., 2016; Zhang et al., 2008):

$$E_r(X) = \frac{1}{2A} [E_{\text{slab}}^{\text{relax}}(X) - E_{\text{slab}}^{\text{unrelax}}(X)] \quad (5.1)$$

When the crystal is cleaved along any plane, surfaces with two terminations are formed simultaneously, dividing the cleavage energy evenly among the two new surfaces. As a result, the respective two terminations will have the same cleavage energy. The cleavage energy E_c can be calculated using the formula:

$$E_c(X,Y) = \frac{1}{4A} [E_{\text{slab}}^{\text{unrelax}}(X) + E_{\text{slab}}^{\text{unrelax}}(Y) - nE_{\text{bulk}}] \quad (5.2)$$

where $E_{\text{slab}}^{\text{relax}}$, $E_{\text{slab}}^{\text{unrelax}}$ and E_{bulk} are the energies of the relaxed slab, unrelaxed slab and the bulk crystal respectively. The n term denotes the number of bulk unit crystals in the resultant slabs. The area of the surface is denoted by the letter A . In Equation 5.1, considering that two surfaces are produced (top and bottom), a coefficient of 2 is introduced in the denominator. The appearance of 4 in Equation 5.2 can be explained from the fact that two surface slabs of X and Y are now considered for calculation after cleaving the bulk structure to form surface slabs. The surface energy (E_{surf}) of each of the slabs can be obtained by adding Equation 5.1 and Equation 5.2.

$$E_{\text{surf}}(X) = E_r(X) + E_c(X,Y) \quad (5.3)$$

The calculated surface energies are plotted in Figure 5.3 for comparison. The surface slab with CuTa surface terminations results in the highest surface energy of about $0.122 \text{ eV}/\text{\AA}^2$, indicating that this structure is the most unstable among the slabs considered. Meanwhile, CuCu surface termination is predicted to be the most stable. Further, the figure also indicates that surface slabs with CuCu and TeTe(1) terminations are significantly more stable than CuTa and TeTe(2) surface terminations. Even though there are significant differences in the level of stability, all the free-standing surface slab models in this work are predicted to be stable since all the surface energies are positive. As already pointed out in the previous section, the outermost atomic layer in TeTe(2) surface terminations is the only surface that relaxed outward. This appears to contradict one of the important criteria of stability. This surprisingly anomalous behaviour of TeTe(2) surface slab is discussed separately in the later section.

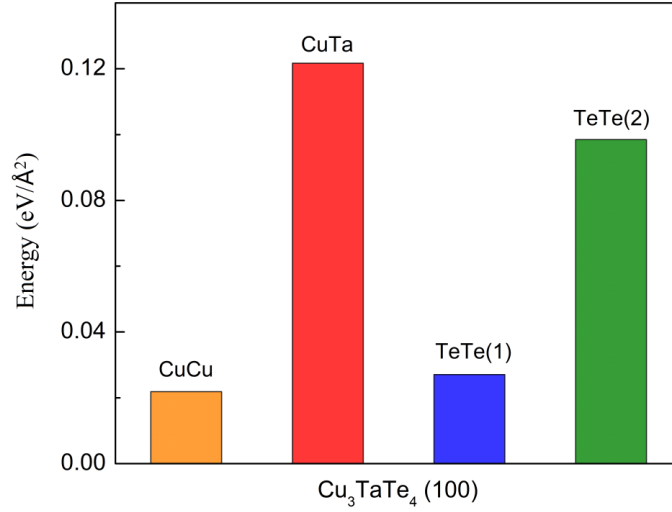


Figure 5.3. Calculated E_{surf} of $\text{Cu}_3\text{TaTe}_4(100)$ surface demonstrating relative stabilities of the four symmetric terminal surface slabs.

Molecular dynamics (MD) simulation is performed for the most energetically stable surface slab of CuCu terminations to verify its thermal stability for potential practical fabrication. The MD simulation is based on two classical assumptions that (i) Newton's laws of motion are obeyed by all interacting atoms and (ii) superposition theorem is satisfied (Alder & Wainwright, 2004; Karplus & McCammon, 2002; Levitt & Lifson, 1969; Zhao et al., 2018). The nVT canonical ensemble approach where the number of atoms (n), volume (V), and temperature (T) are constrained is implemented for the simulation. The energy time evolution at room temperature as predicted from the MD simulation is shown in Figure 5.4. It is observed that throughout the process, energy remains almost constant with maximum energy difference of about 3 kJ/mol only. The absence of drastic energy change indicates the possible dynamical stability even at room temperature. Besides this prediction, from a practical standpoint, the application of non-equilibrium epitaxial thin film growth has been reported to be able to handle volatility of the surfaces if any exists.

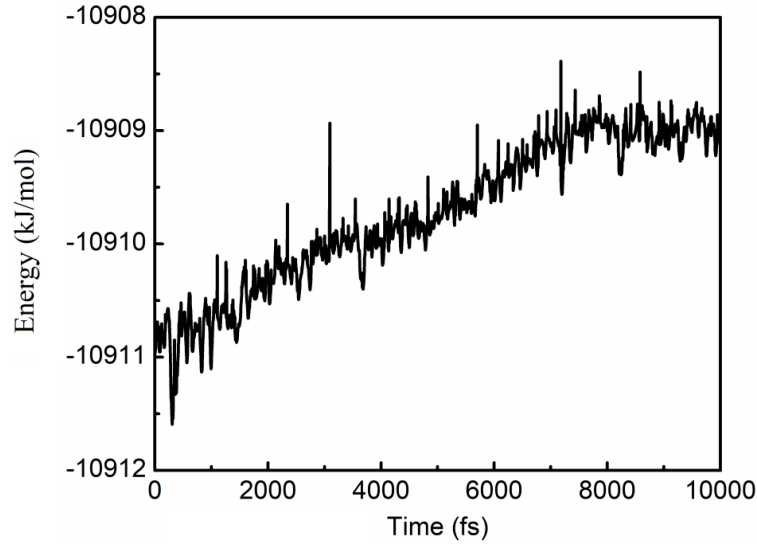


Figure 5.4. Energy-time evolution of CuCu terminated surface slab illustrating thermal stability with maximum energy difference of 3 kJ/mol within 10000 fs.

5.5 Surface electronic and magnetic properties

Electronic band structure along with the corresponding DOS of the four conventional $\text{Cu}_3\text{TaTe}_4(100)$ slab models with all possible symmetric terminations are shown in Figure 5.5 to Figure 5.8. In agreement with reported literature (Lalrinkima et al., 2022), when cleaving the bulk structure and reducing the material into few atomic layers, semiconducting nature is no longer maintained. The electronic band structure of the slab models with CuCu and CuTa surface terminations (Figure 5.5 and Figure 5.6) exhibit half metallic (HM) behaviour with energy gap for spin-down channel and metallic nature for spin-up channel. Meanwhile, both the slab models with TeTe(1) and TeTe(2) terminations (Figure 5.7 and Figure 5.8) exhibit metallic behaviour. The HM nature exhibited by surface slabs with CuCu and CuTa terminations indicates that these materials could be suitable for spin-polarized injection of charge carriers.

Figure 5.5 shows that atomic orbitals (mostly d-orbitals of Cu and Ta) from the core and σ -2 subsurface/ atomic layer are the primary contributors near the Fermi energy. Thus, the outermost atomic layer consisting of Cu atoms and the σ -2 atomic

layer governs the HM property in this surface slab. Whereas, in the surface slab with CuTa termination as shown in Figure 5.6, atomic orbitals from the outermost σ surface (mostly d-orbitals of Cu and Ta) and the adjacent subsurface σ -1 atomic layer (mostly p-orbitals of Te) act as the major contributors for the energy states near the Fermi energy. Further, the DOS plots for the two slab models also predict that the metallic nature in these materials is mostly due to atomic orbitals from the σ surface and σ -2 subsurface (mostly d-orbitals of transition metals) crossing the E_F .

From corresponding DOS plots for surface slabs with TeTe(1) and TeTe(2) terminations (Figure 5.7 and Figure 5.8). Not only that these two surface slabs not exhibit spin polarization, the energy states from valence band atomic orbitals clearly crosses the E_F , thus confirming the fully metallic nature as seen in the electronic band structure. The DOS plots also indicate that all atomic layers (surface, subsurface, and the core region) contribute to the fully metallic nature in these two surface slabs.

It is also noteworthy that the extent by which the energy states arising from atomic orbitals cross the E_F is quite small in the case of surface slabs with CuCu and TeTe(1) terminations. It may be possible to transform these two systems into either p-type or n-type semiconductors through surface passivation with gas molecules. This could open another avenue for exploring the surface slabs for novel device applications.

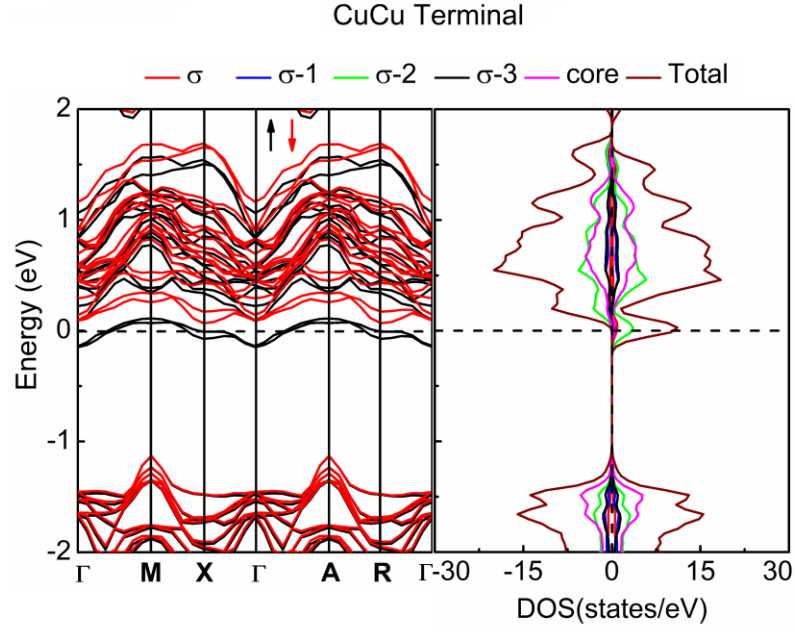


Figure 5.5. $\text{Cu}_3\text{TaTe}_4(100)$ surface slab with CuCu terminal exhibiting HM with metallic nature for spin-up channel and semi conducting nature for spin-down channel.

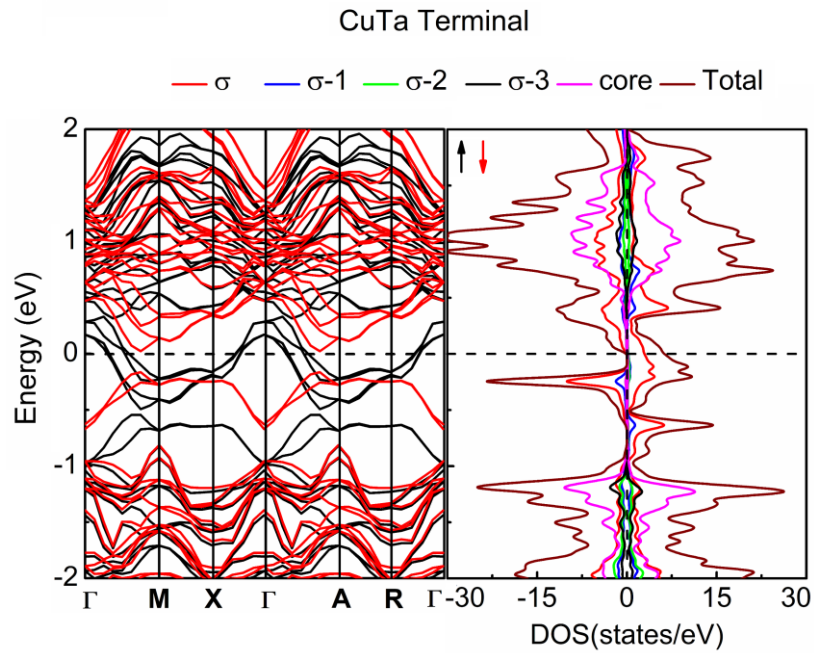


Figure 5.6. $\text{Cu}_3\text{TaTe}_4(100)$ surface slab with CuTa terminal exhibiting HM with metallic nature for spin-up channel and semi conducting nature for spin-down channel.

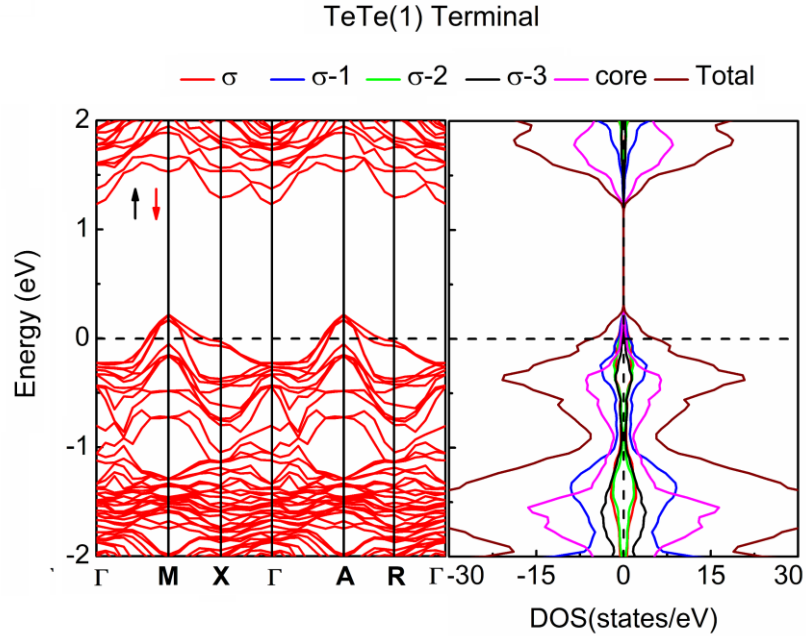


Figure 5.7. $\text{Cu}_3\text{TaTe}_4(100)$ surface slab with TeTe(1) terminal exhibiting metallic nature for both spin-up and spin-down channel.

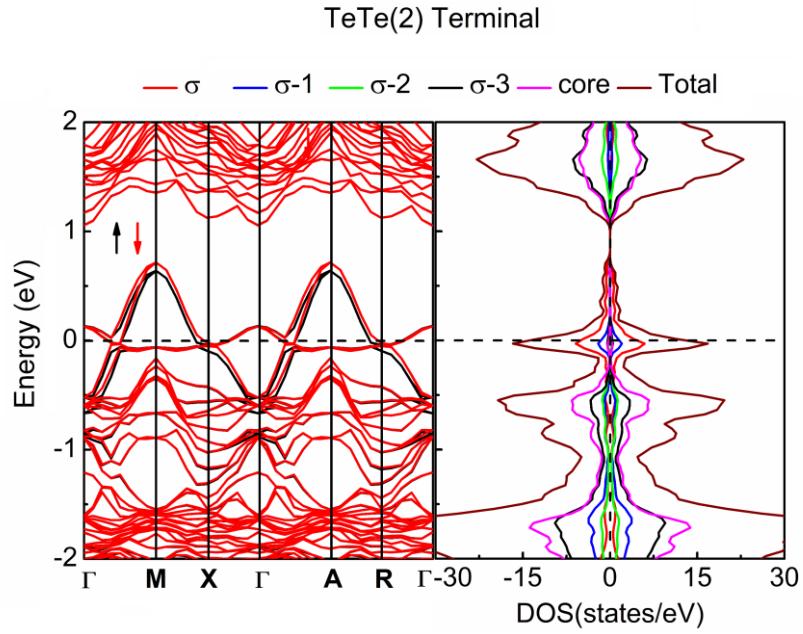


Figure 5.8. $\text{Cu}_3\text{TaTe}_4(100)$ surface slab with TeTe(2) terminal exhibiting metallic nature for both spin-up and spin-down channel.

The atomic magnetic moments and Bader charge transfer per atom of $\text{Cu}_3\text{TaTe}_4(100)$ surface (σ) and sub-surfaces (σ -1, σ -2, σ -3) of the four slab models are given in Table 5.2. Since slab models with TeTe terminations do not exhibit spin polarization, they do not possess any magnetic moment and, therefore, are not shown in the table. Meanwhile, surface slab models with CuCu and CuTa terminations exhibit ferromagnetic behaviour due to spin polarization of charges. The magnetic moment contributions from each atomic layer given in the table shows that Ta atoms are the main contributors. The net magnetic moment, including contributions from the core atoms amount to $1.0 \mu_B$ and $3.0 \mu_B$ in surface slabs with CuCu and CuTa terminations respectively. Interestingly, the main difference in the net magnetic moment in these two systems appears to be a result of the difference in magnetic moment per atom of Ta when it is located at the surface and at the deeper atomic layer. Magnetic moment for each Ta atom at the surface is significantly higher than when it is at the σ -2 atomic layer. This enhanced magnetic moment of surface atoms could be due to the difference in Bader charge transfer and the presence of dangling bonds at the surface (Henkelman et al., 2006; Tang et al., 2009). In Table 5.2, the transition element Te behaves as anion and gains charges while Cu and Ta elements lose charges. However, depending on the location of ions and the termination, the charge transfer per atom varies.

Table 5.2. Calculated atomic magnetic moments (in μ_B) and Bader charge transfer in the four conventional slab models of $\text{Cu}_3\text{TaTe}_4(100)$.

$\text{Cu}_3\text{TaTe}_4(100)$					
CuCu	Surface	Cu(σ)	Te(σ -1)	Cu/Ta(σ -2)	Te(σ -3)
	Magnetic moment	0.029	0.001	0.003/ 0.198	-0.004
	Bader charge	0.1038e	-0.3819e	0.0956e/ 1.2249e	-0.3926e
CuTa	Surface	Cu/Ta(σ)	Te(σ -1)	Cu(σ -2)	Te(σ -3)
	Magnetic moment	0.005/0.696	-0.001	0.037	0.004
	Bader charge	-0.0187e / 0.7208e	-0.3339e	0.0601e	-0.3870e
TeTe(1)	Surface	Te(σ)	Cu/Ta(σ -1)	Te(σ -2)	Cu(σ -3)
	Bader charge	-0.3861e	0.1091e / 1.2594e	-0.3800e	0.0929e
TeTe(2)	Surface	Te(σ)	Cu(σ -1)	Te(σ -2)	Cu/Ta(σ -3)
	Bader charge	-0.0670e	0.1415e	-0.3570e	0.0996e / 1.2505e

5.6 Surface reconstruction in TeTe(2) surface slab terminal

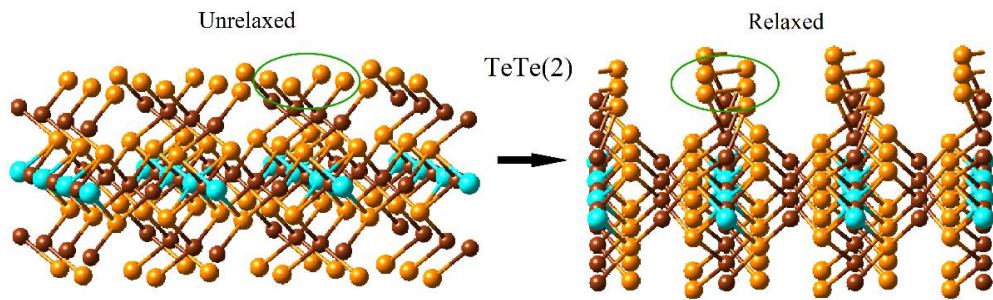


Figure 5.9. TeTe(2) surface before and after relaxation illustrating possible Te-Te bonding, leading to surface reconstruction.

The surface slab with TeTe(2) surface slab termination requires further investigation due to its outward relaxation while all the other three terminations relaxed inwards. When the bulk crystal is cleaved along (100) plane to obtain TeTe(2) termination, the other side of the cleaved surface will form CuTa termination, thus,

these two surfaces are considered as surface cleavage counterparts. Out of these two surface terminations, CuTa relaxed inwards while TeTe(2) surface relaxed outwards. Therefore, CuTa surface is expected to be more stable than TeTe(2) surface. However, the surface energy calculation in section 5.4. concluded that TeTe(2) surface is relatively more stable than CuTa surface. Due to this seemingly contradicting result, we analyse the TeTe(2) and other surface terminations. Interestingly, we found that surface recombination takes place with chemical bond formation between Te atoms in the case of TeTe(2) terminations, as shown in Figure 5.9, which is missing in other surface slab models. In the figure, the structure of the surface slab considered is same as the structure displayed in Figure 5.2. The only difference is that in Figure 5.9 larger supercell along the plane is considered for better visual understanding. No separate DFT calculation is performed. The larger supercell shows periodic repetition along the plane so that the surface before and after relaxation can be examined for any variation.

In addition to surface visualization, further analysis is performed to ascertain the possible surface reconstruction in TeTe(2) termination. Total energy before and after relaxation is calculated for all the surface slab models. The surface slab model with TeTe(2) termination has an unrelaxed total energy of -124.15 eV, and after relaxation, it became more stable with total energy of -127.03 eV. The difference in energy after relaxation is -2.88 eV, which is significantly larger than the corresponding energy difference in other slab models (less than -2 eV). This indicates that the relaxation in the surface slab model with TeTe(2) termination involves certain mechanism, which effectively reduces its total energy. The possible phenomena that effectively reduce the total energy could be chemical bonding formation among Te atoms at the surface. The experimentally observed Te atomic radius is reported to be 1.23 Å (Clementi et al., 2004), and our calculated distance between two Te atoms before ($d_i^{\text{Te-Te}}$) and after ($d_f^{\text{Te-Te}}$) relaxation at the surface (σ) are 4.356 Å and 2.695 Å (or 1.347 Å Te atomic radii) respectively. This decrease in distance of 1.661 Å corresponds to 38.13% of the unrelaxed separation. This observation indicates that the atomic separation between Te atoms may be within the potential bond formation after structural relaxation (Burns & Gillespie, 1982; Kim et al., 2006; Saethre & Gropen, 1992).

5.7 ELF for TeTe(2) terminal surface slab

The probability of discovering an electron in the vicinity space of a reference electron with the same spin and location is determined by the electron localization function (ELF) (Savin et al., 1992; Silvi & Savin, 1994). The ELF is expressed using Equation 2.50 to Equation 2.53. Considering the theoretical knowledge as presented in section 5.6, we calculate ELF for the surface slab with TeTe(2) termination to make a reliable prediction in the surface reconstruction process. Figure 5.10 shows the ELF surface plot of the surface slab. The scale plotted in the figure corresponds to the colour coding. The red colour corresponds to high ELF value, and the green colour corresponds to low ELF value or even absence of electron in the vicinity. Since Te behaves as anion in the structure, ELF at the location of each of the Te atom is represented with red colour cloud. The two Te atoms in the inner atomic layers are clearly separated. However, the two Te atoms at the surface (top of the structure in the figure) are joined with slightly reddish thin yellow colour. From the colour coding, the ELF value corresponding to this colour can be interpreted as somewhere between 0.5 and 0.7. This indicates the presence of delocalized electrons, presumably metallic bonding between the two Te atoms. At the bottom most atomic positions, a solid circle appears, indicating the same Te-Te chemical bonding. This seeming variation in graphical representation is due to the alignment of Te-Te atoms. The alignment is such that the orientation is along the contour plane at the top most position while it is perpendicular to the plane at the bottom most atomic position. Since, the ELF corresponding to Te atoms within the inner atomic layers are clearly separated, it shows that there is no chemical bonding between them. These observations lead to our conclusion that surface reconstruction process indeed occurs in surface slab with TeTe(2) terminations and is thus relatively more stable than its surface counterparts, the surface slab with CuTa termination.

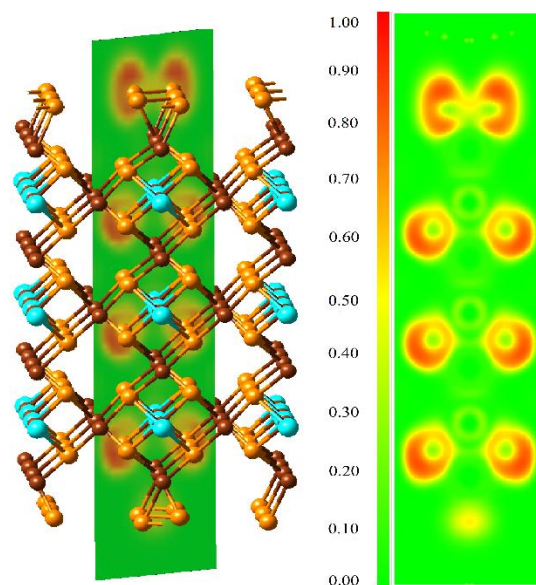


Figure 5.10. ELF surface plot of TeTe(2) terminal demonstrating Te-Te bonding due to surface cleavage, leading to surface reconstruction, resulting in more stability than its CuTa cleavage counterpart.

CHAPTER 6
SUMMARY AND CONCLUSION

6

Summary and conclusion

This chapter will contain all the *ab initio* results of selected Cu_3MX_4 compounds as anticipated. We have successfully investigated the bulk, doped, and surface slab properties of the compounds from theoretical insights along with their application prospects, where our study result outlines new findings due to our novel research approach as compared to the numerous existing literatures. Also, just as our research puts its main emphasis on the photovoltaic and thermoelectric prospects for green energy harvesting, our results put more stress on these properties from both the bulk and doped structures, while basic properties are explored in surface slab models due to their non semiconducting nature. The following below the conclusions we have drawn from our study:

- We have explored the structural, mechanical, electronic, dynamical stability, optical, and thermoelectric properties of Nb-based copper sulvanite compounds Cu_3NbX_4 ($\text{X}=\text{S}, \text{Se}, \text{Te}$) at 0, 5, 10, 15, and 20 GPa isotropic pressure within the framework of DFT and semi-classical Boltzmann transport equation. Our calculated results are in good agreement with experimental data, especially in their lattice parameters; 5.54, 5.72, and 6.00 Å respectively for $\text{X}=\text{S}, \text{Se},$ and Te at 0 GPa, subsequently reduced in lattice parameters with induced compressive pressure. Mechanical properties within Hill's assumption confirm Cu_3NbX_4 's non-ductile nature, which is consistent with previously reported data. Also, dynamical stabilities of the investigated compounds are verified through phonon calculations, where absence of negative phonon frequencies at all the pressures validates stability. Dynamical stability is of special importance as it essentially determines whether predicted materials are physically realizable; as such, Cu_3NbX_4 should exist under such pressures for synthesis. Also, doping investigation on $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ exhibits quite similar

mechanical properties to their bulk counterpart where non-ductile nature is observed at all doping levels from Poisson's and Pugh's ratio. In the 2x2x2 supercell containing 64 atoms, phonon calculation becomes impractical in our low-end computational device. As such, thermal stability is investigated from formation energy calculations and was verified for all the supercells, validated by negative formation energies.

The structural and mechanical properties approach in surface slabs of $\text{Cu}_3\text{TaTe}_4(100)$ is unique to its bulk counterpart. All possible symmetric terminals of CuCu, CuTa, TeTe(1), and TeTe(2) are investigated with thickness of 17.4, 17.4, 21.2, and 22.3 Å, respectively, consisting of 13-15 atomic layers. The method of surface energy calculations is employed for stability examination, and surface slabs with CuCu terminal is the most stable while CuTa is relatively the least stable. Moreover, surface reconstruction is observed in TeTe(2) terminal from ELF calculations, possibly resulting in enhanced stability than its CuTa surface counterpart.

- The electronic properties result reveals moderate energy band gaps, ranging from 2.23 – 1.02 eV for Cu_3NbX_4 within the GGA formalism with U correction and SOC, which further diminish with pressure, attaining the lowest 1.67 – 0.22 eV at 20 GPa. Indirect band gap semiconductor nature is observed where the VBM and CBM are located at the R and X symmetry points of the first Brillouin zone, respectively. The *ab initio* U values are practically independent of applied pressures with ~ 11 eV for Cu-d and ~ 3 eV for Nb-d orbitals. The d-orbitals of Nb persist as the main contributor to the CB near the Fermi level E_F (=0 eV) with minor contributions from possible hybridized states of X-p and Cu-d orbitals from PDOS analysis. In the VB, all possible hybridized states from p-orbitals of chalcogenide atoms, Nb-d and Cu-d orbitals contribute near the E_F while Cu-d orbitals persist to be the dominant contributor in the deeper energy bands. The predicted energy band gaps for $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercells are 1.68, 1.29, 1.13, 1.08, and 1.03 eV for X=0.00, 0.25, 0.50, 0.75, and 1.00 respectively. Direct/indirect band gap nature, however, cannot be realized due to band folding. The abrupt decrease from 1.68 eV to 1.29 eV occurs due to V atom, which is identified to be the main cause. As such, gradual decrease in band gaps can be comprehended from the increasing V concentration.

- Investigations into optical properties reveal interesting properties both from Cu_3NbX_4 and $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$. The absorption coefficient (α), deduced from the real part (ϵ_1) and imaginary part (ϵ_2) of refractive index, yields promising results. The optical band gap ranges from 2.74 – 1.85 eV for Cu_3NbX_4 and 2.11 – 1.53 eV for $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$; was determined from the onset of optical activities as similar to experimental approach. For Cu_3NbX_4 , narrowing of optical band gaps from 2.39 – 1.28 eV continues with pressure. From both pressure and doping investigations, it is evident that certain optical band gap lies within the optimum range of ~ 1.5 eV for photovoltaic prospects, especially as photovoltaic absorbers. Furthermore, the optical band gaps are also consequently red-shifted with enhanced absorption coefficient of $\sim 10^5 \text{ cm}^{-1}$ in the IR-vis region, which further suggests for enhanced photovoltaic absorber prospects.

- Thermoelectric prospects of Cu_3NbX_4 and $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ are successfully examined through the semi-classical Boltzmann transport equation utilizing the BoltzTraP code and Slack's equation. While following the same fundamental principle, a different approach, namely CRTA and RTA is utilized for $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ and Cu_3NbX_4 respectively. In CRTA, default relaxation time $\tau = 10^{-14} \text{ s}$ is considered for calculations while τ obtained from exploiting deformation potential for each compound is used in RTA, which still remains in the order 10^{-14} s with certain multiplication factors. Though transport parameters like Seebeck coefficient (S) and electrical conductivity (σ) decrease and increase respectively with pressure in general, the power factor PF remains almost independent of pressure. The maximum thermoelectric figure of merit ZT for X=S, Se, and Te, respectively, are obtained to be 0.58, 0.26, and 0.48. Doping investigations exhibit interesting transport elements unique to doping. As the Seebeck coefficient decreases with V doping concentration, the σ is greatly enhanced in magnitude in the p-type doping while greatly reduced in the n-type doping. Interestingly, though such phenomenon occurs, ZT for p-type and n-type doping remains almost the same due to the fact that when σ is reduced in n-type doping, correspondingly decrease in κ_e which enhances ZT. As such, ZT values of ~ 0.8 are obtained at all doping levels with maximum values of 0.83 exhibited by $\text{Cu}_3\text{Nb}_{0.25}\text{V}_{0.75}\text{S}_4$ and Cu_3VS_4 at 1100K, exhibiting prospects for potential thermoelectric materials.

- The $\text{Cu}_3\text{TaTe}_4(100)$ surface exhibit properties unique to its bulk Cu_3TaTe_4 counterpart especially in electronic related properties. Though bulk Cu_3TaTe_4 demonstrates semiconducting nature with net zero magnetism, $\text{Cu}_3\text{TaTe}_4(100)$ surface exhibits either metallic or half-metallicity depending on the various symmetric terminals of CuCu, CuTa, TeTe(1), and TeTe(2). Half-metallicity is revealed by CuCu and CuTa terminals with $1.0 \mu_B$ and $3.0 \mu_B$ net magnetic moment respectively. The CuCu surface slab terminal especially could hold promising spintronics application prospects owing to it being the most stable surface terminal.

We conclude our investigation of copper sulvanite compounds, which showed promising characteristics, particularly as a photovoltaic absorber layer for solar cell applications, owing to the high absorption coefficient of the order $\sim 10^5 \text{ cm}^{-1}$. These characteristics were further enhanced by certain pressure and doping, which redshifted the band gaps where visible part of incident radiation could be significantly absorbed for the production of photoelectrons. Additionally, the stability of the compounds under investigation is tested and verified using a variety of techniques, indicating that they are not merely theoretical but possess real-world applications. Furthermore, the moderate thermoelectric efficiency $ZT \sim 0.8$ could be improved by lowering thermal conductivity or by enhancing a constituent element associated with ZT . All these discoveries suggest the investigated compounds for promising green energy harvesting. Interesting half-metallic characteristics are observed for surface slabs, which should contribute significantly to spintronics technology.



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LIST OF PUBLICATION AND ACTIVITIES

I. Journals:

1. **Bernard Lalroliana**, Lalmuanchhana, Lalthumhima, Lalrinkima, Shivraj Gurung, Y. Rangeela Devi, Ningthoujam Surajkumar Singh, Zodinmawia, Dibya Prakash Rai, Lalhriatzuala (2023). Ab initio prediction of half-metallicity, stability and reconstruction in Cu₃TaTe₄ (100) surface. *Computational Materials Science*, 230, 112476, <https://doi.org/10.1016/j.commatsci.2023.112476>. ISSN 0927-0256.

2. **Bernard Lalroliana**, Lalmuan chhana, Lalthum hima, R. Zosiamliana, Shivraj Gurung, Lalhriat zuala (2024). Nb-based copper sulvanites for potential green energy harvesting under induced isotropic pressure. *Materials Research Bulletin*, 180, 2024, 113054, <https://doi.org/10.1016/j.materresbull.2024.113054>. ISSN 0025-5408.

3. **Bernard Lalroliana**, Lalmuanchhana, Lalthumhima, L. Celestine, Dibya Prakash Rai, Lalrinthara Pachuau, N. Surajkumar Singh, Shivraj Gurung, Lalhriatzuala (2025). Enhanced optical and thermoelectric properties of Cu₃Nb_{1-x}V_xS₄ through chemical substitution: a DFT approach. *New Journal of Chemistry*, 49, 1763-1772, <https://doi.org/10.1039/D4NJ04230A>. ISSN 1144-0546.

II. Conferences/Workshop Attended

(a) National:

1. 4th Mizoram Science Congress, 24th – 25th November, 2022, Mizoram Science, Technology, and Innovation Council (MISTIC), Aijal Club, Aizawl (**Oral presentation**).

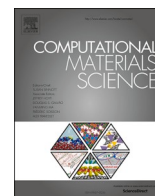
(b) International:

1. Virtual International Conference on Functional Materials & Applied Physics (FMAP-2022), 14th – 15th October, 2022, Department of Physics, Sardar Vallabhbhai National Institute of Technology, Surat (**Online presentation**).

2. 7th International Conference on Nanoscience and Nanotechnology (ICONN-2023), 27th – 29th March, 2023, Department of Physics and Nanotechnology, SRM IST, India (**Online presentation**)

3. International Conference on Recent Advances in Mathematical, Physical, and Chemical Sciences (ICRAMPC-2024), 21st – 23rd February, 2024, School of Physical Sciences, Mizoram University, Aizawl, Mizoram (**Oral Presentation**)

4. Exploring the complexities of Physical and Earth System dynamics through modeling and data analysis, 27th – 29th February, 2024, School of Physical Science, Pachhunga University College, Mizoram (**Oral presentation**).



Full Length Article

Ab initio prediction of half-metallicity, stability and reconstruction in Cu_3TaTe_4 (1 0 0) surface

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ABSTRACT

This study reports DFT calculations on structural stability, electronic and magnetic properties of $\text{Cu}_3\text{TaTe}_4(100)$ surface. Four possible symmetric terminations such as CuCu, CuTa, TeTe(1), and TeTe(2) are considered in cleaving the bulk crystal along (1 0 0) plane to form surface slab models. Surface energy calculation predicts that surface slab with CuCu termination is most stable and CuTa termination is most unstable. Meanwhile, the structural parameters after relaxation indicate that TeTe(2) surface could be most unstable due to its outward relaxation. Electron Localization Function calculations have shown that this seemingly contradicting results could be due to surface reconstruction in TeTe(2) surface, which significantly lowers the energy of the system. Electronic band structures of $\text{Cu}_3\text{TaTe}_4(100)$ surface slabs exhibit transition from semiconducting nature in bulk crystal to either half metallic or fully metallic nature depending on the termination. The half metallic nature in CuCu and CuTa surface terminations provide promising theoretical data for future development of spintronic device.

1. Introduction

Materials with diverse functional properties have always fascinated academicians and researchers. An extensive exploration on bulk copper sylvanite compounds (Cu_3TMX_4 : TM = V, Nb, Te; X = S, Se and Te) have been pursued both in theory and experiments [1–4]. In their bulk form, all the sylvanite compounds are found to be indirect band gap semiconductors showing promising properties as potential photovoltaic absorber, photo catalysts for water splitting, good thermoelectric materials, etc [5–10]. However, scaling down from bulk to nanoscale is required for device fabrication and realization. The significance of nanostructures such as thin films and nanoparticles is well known since they are the main drivers of ongoing technological advancements in optoelectronic, photonic, and magnetic devices, [11,12]. Also, several new fields of inquiry in solid state physics and chemistry have been advanced through thin film studies characterized by thickness, geometry, and structure. In developing thin films, the bulk sylvanite compounds are reduced to few atomic layers, thereby resulting in significant deviation of most properties from their bulk counterparts [13,14]. This

makes study of surface properties interesting and thus motivates this work.

In the experimental aspect, Lv *et al.*, [15] have successfully prepared nano- Cu_3VS_4 thin film of thickness 220 nm by pulsed laser deposition (PLD) method. Using spectroscopic ellipsometry, the optical band gap is found to be 1.35 eV, which is within acceptable range for potential photovoltaic absorber. Subsequently, Syu *et al.*, [16] developed a solar cell based on these thin films with 3.11% efficiency. Liu *et al.*, [17] have also reported Cu_3VSe_4 nanosheets having thickness of 604 nm with 1.8 eV optical band gap. Further, Newhouse *et al.*, [18] have designed Cu_3TaS_4 and Cu_3TaSe_4 thin films of 200 nm thickness having band gap of 2.70 and 2.35 eV respectively using the two-step growth technique involving PLD and *ex-situ* annealing. In all these studies, copper sylvanite compounds have been reported to have (100) preferential growth direction.

Despite various experimental studies with promising results, there is no theoretical study on the surface properties of copper sylvanite compound thin films till today. However, surface properties have been reported to play a vital role in determining the property of thin films as a

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whole [19–25]. So, in the present work, we investigate Cu_3TaTe_4 (100) surface properties by modelling a free-standing slab along z-axis from the optimized Cu_3TaTe_4 bulk structure. To make our study systematic, we consider only symmetric terminations with CuCu, CuTa, TeTe(1), and TeTe(2) atoms at the surface. The bulk and surface electronic properties are then analysed and compared. Further, surface energy of each termination is calculated to examine their stabilities for possible practical fabrication. Lastly, a more thorough investigation is conducted to verify assertions on the anticipated possibility of surface reconstruction in TeTe(2) surface terminal.

2. Computational details

The first principles calculations were carried out using spin polarized density functional theory (DFT) [26,27], based on the projector augmented wave (PAW) [28–31] approach as implemented and programmed in MedeA-Vienna *ab-initio* Simulation Package (VASP). It has been reported that hybrid functionals like B3LYP and B3PW can predict band gaps in excellent agreement with experiments [32,33]. To take care of the computational costs and time for our low end computational device, electron correlation exchange energy within the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) [34] formalism is used to treat all electron interactions. For the bulk and (100) surface, plane wave kinetic energy cutoff was set to 400 eV. The self-consistent field calculation steps were carried out until the energy difference is less than 10^{-5} eV. To study stability and electronic properties of Cu_3TaTe_4 (100) surface, surface slab models having 13/15 atomic layers with four different symmetrical terminations CuCu, CuTa, TeTe(1) and TeTe(2) along (100) plane have been built. Structural optimizations were accomplished with the conjugate gradient technique with a force tolerance of 0.01 eV/Å. The explicit k-mesh chosen for bulk and surface calculations are $8 \times 8 \times 8$ and $10 \times 10 \times 1$ Monkhorst pack grid [35] respectively. For electronic properties calculation, an even denser k-mesh of $12 \times 12 \times 1$ is sampled to integrate first 2D Brillouin Zone.

3. Results and discussion

3.1. Bulk Cu_3TaTe_4

The conventional cubic crystal structure (P-43m symmetry group) of Cu_3TaTe_4 is shown in Fig. 1. Cu atoms occupy the bisection points of the lattice lengths in the Wyckoff's position 3d(0.5, 0, 0); Ta atoms at the eight corners of the cube and four Te atoms located wholly inside the crystal and their Wyckoff's positions are 1a(0, 0, 0) and 4e(x, x, x) respectively. After optimization, the lattice parameter is 6.007 Å which have a relative error of about $\pm 1.30\%$ only as compared to values from experiment [36]. A slight overestimation of our calculated lattice

constant is typical for GGA approach [37,38]. Good agreement in calculated lattice parameter with experimental value validates the consistency of our bulk structure calculations and its suitability for further surface investigation.

Before proceeding to surface properties, electronic properties of the bulk crystal are first calculated and presented in Fig. 2. The electronic band structure shows indirect band gap semiconducting nature with conduction band minima (CBM) and valence band maxima (VBM) located at the X and R high symmetry points respectively. The energy band gap value obtained 1.16 eV is consistent with reported results obtained using DFT calculations with GGA-PBE functional [39]. Further, DOS of the bulk structure shows symmetry around the Fermi Energy (E_F) for both spin up and spin down channel, thus, revealing the nonmagnetic nature of the compound with net zero spin polarization. The PDOS plot shows that the energy states near the conduction band edge mainly originates from Ta-d orbitals while the corresponding energy states in the valence band (VB) are mainly due to hybridization of Cu-d and Te-p.

3.2. Surface and structural relaxation

Conventional (100) symmetric surface slab models of Cu_3TaTe_4 considered for this work are shown in Fig. 3. This is done so as to eliminate any unfavourable induced polarization caused by unsymmetrical surface terminations [19]. To achieve symmetric terminations, the surfaces are cleaved at different thicknesses depending on the terminations chosen. This results in different number of atomic layers. While there are only 13 atomic layers for both CuCu and CuTa surface terminations, there are 15 atomic layers for both TeTe(1) and TeTe(2) surface terminations. To avoid interactions from the neighbouring periodic repetitions along the z axis, a vacuum of 15 Å [22] is applied on both the top and bottom surfaces. When performing structural optimization, only the first four outer atomic layers on either side of the surfaces are relaxed [22,40] while the remaining inner atomic layers, i.e., 5 central layers for CuCu and CuTa surface terminations and 7 central layers for TeTe(1) and TeTe(2) surface terminations are considered as core region and atoms are fixed such that they resemble their bulk positions. This approach is followed to achieve optimization without significant loss to accuracy.

Structural parameters after relaxation are given in Table 1. When considering surface atoms, reduction of coordination numbers occurred due to the breaking of translational symmetry. This usually results in either contraction or expansion of inter atomic distances to minimise energy. In Table 1, d denotes distance between adjacent atomic layers shown in Fig. 3. Atomic layers of surface slab models are identified with the Greek letter σ in Table 1. Here, σ represents the outermost atomic layer, which is the atoms at the surface. $\sigma-1$ represents the immediate subsurface atomic layer just beneath the surface. $\sigma-2$ and $\sigma-3$ represents the deeper subsequent subsurface atomic layers. The subscripts i and f in

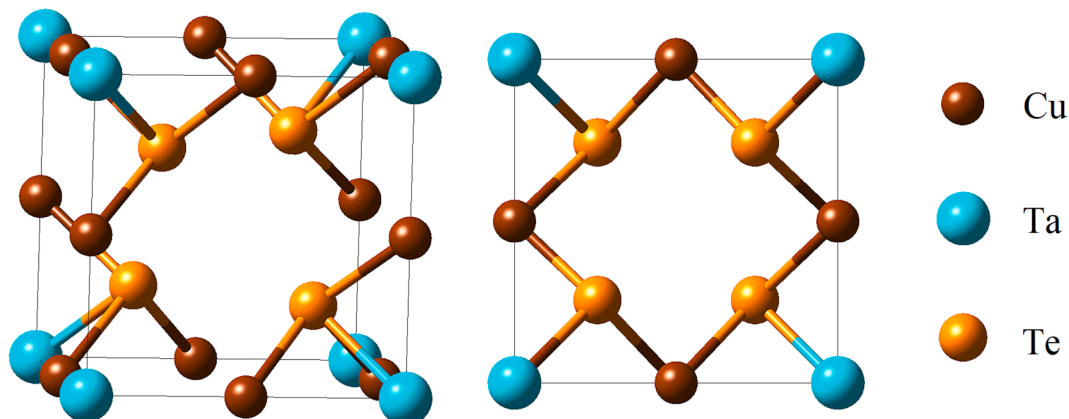


Fig. 1. Crystal structure of Cu_3TaTe_4 (side view and top view).

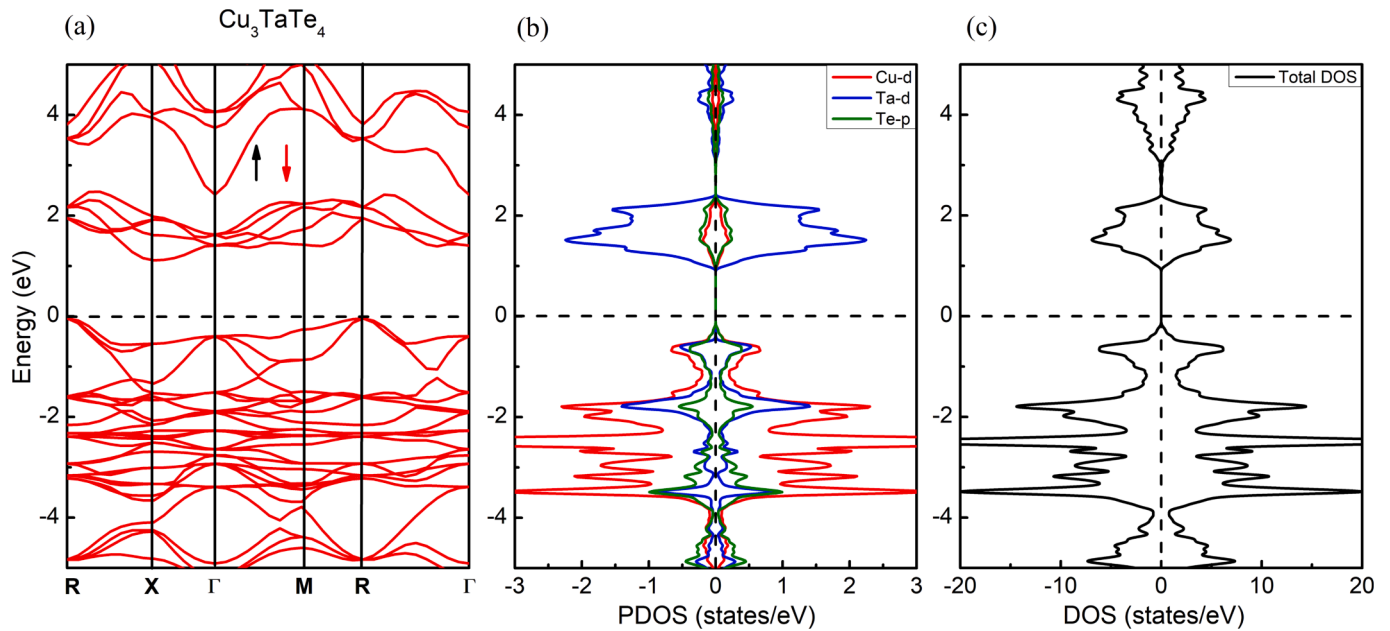


Fig. 2. Bulk Cu_3TaTe_4 (a) electronic band structure (b) PDOS (c) DOS.

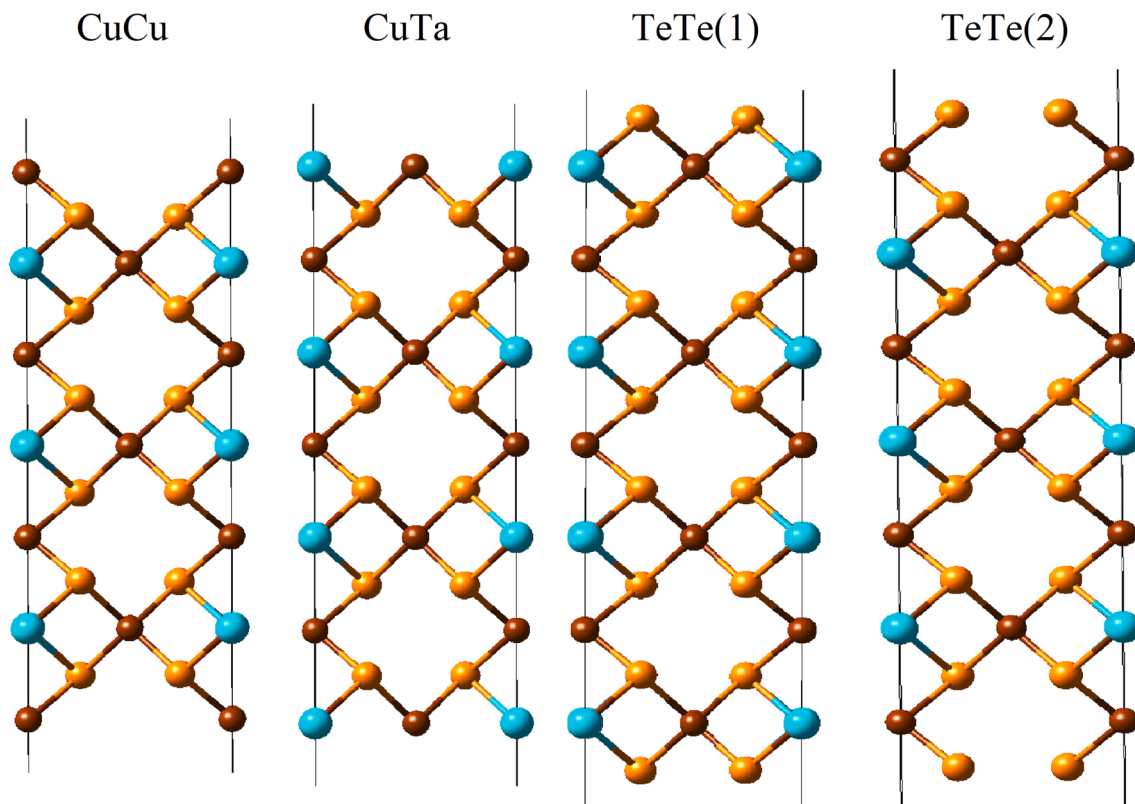


Fig. 3. Conventional slab models of $\text{Cu}_3\text{TaTe}_4(100)$ surface.

the table denote before and after relaxation respectively. Thus, $\Delta d_{f-i} = d_f - d_i$ represents the changes in interatomic distances between atomic layers after relaxation. Positive value of Δd_{f-i} represents expansion and negative value of Δd_{f-i} represents contraction. The percentage changes given in the table are calculated with respect to bulk lattice parameter. Except for the TeTe(2) termination, it is observed that all the three other terminations exhibit compression of the distance between atomic layer at the surface and the adjacent subsurface. However, the extent of

compression varies from one termination to another with 6.16, 3.44, and 0.20 % for CuCu, CuTa and TeTe(1) surface terminations respectively. This inward relaxation of the outermost surface indicates potential of the slab to hold the outermost atomic layer, which is an important criterion for stability of a surface. In addition, the three surface terminations follow the same trend of alternatingly decreasing and increasing inter layer separation after relaxation when moving deeper into the subsequent atomic layers. As for the TeTe(2) termination, the distance

Table 1

The four surface terminations of $\text{Cu}_3\text{TaTe}_4(100)$ with calculated slab thickness, layer under consideration, initial d_i and final d_f , change in d after relaxation Δd_{f-i} and percentage change with respect to bulk lattice constant (all distance in units of Å).

Terminal	Slab thickness	Layer	d_i	d_f	Δd_{f-i}	% of Δd_{f-i}
CuCu	17.4	CuCu σ	1.464	1.094	-0.370	-6.16
		TeTe σ -1	1.540	1.613	0.073	1.22
		CuTa σ -2	1.540	1.514	-0.026	-0.42
		TeTe σ -3	1.464	1.489	0.025	0.42
CuTa	17.4	CuTa σ	1.540	1.333	-0.207	-3.44
		TeTe σ -1	1.464	1.534	0.070	1.17
		CuCu σ -2	1.464	1.445	-0.018	-0.31
		TeTe σ -3	1.540	1.554	0.014	0.23
TeTe(1)	21.2	TeTe σ	1.540	1.528	-0.012	-0.20
		CuTa σ -1	1.540	1.570	0.030	0.49
		TeTe σ -2	1.464	1.440	-0.023	-0.39
		CuCu σ	1.464	1.476	0.012	0.20
TeTe(2)	22.3	TeTe σ	1.464	2.245	0.782	13.01
		CuCu σ	1.464	1.346	-0.118	-1.96
		TeTe σ -2	1.540	1.531	-0.009	-0.15
		CuTa σ	1.540	1.551	0.011	0.19

between the outermost atomic layer and the immediate subsurface atomic layer expands drastically by an astonishing amount of 13.01%. This outward relaxation could be attributed to the metallicity of the surface, which could result in the surface atomic layers attempting to reorganise the displaced valence electron density [41]. Apart from this, the two subsurface atomic layers (σ -1, σ -2) undergo contraction by 1.96 and 0.15% respectively while σ -3 surface expands by 0.19%.

3.3. Surface stability

Energetical stability of each of the four surface slab models having different terminations are estimated by calculating the surface energy. This will provide necessary theoretical data for practical realization of thin films with different surface terminations along (100) plane. The surface energy consists of two terms such as the relaxation energy and the cleavage energy. The relaxation energy (E_r), which is the amount of energy required to relax both sides of the surfaces is expressed as [20,42–44]:

$$E_r(X) = \frac{1}{2A} [E_{slab}^{relax}(X) - E_{slab}^{unrelax}(X)] \quad (1)$$

When the crystal is cleaved along any plane, surfaces with two terminations are formed simultaneously dividing the cleavage energy evenly among the two new surfaces. As a result, the respective two terminations will have the same cleavage energy. The cleavage energy E_c can be calculated using the formula:

$$E_c(X, Y) = \frac{1}{4A} [E_{slab}^{unrelax}(X) + E_{slab}^{unrelax}(Y) - nE_{bulk}] \quad (2)$$

where E_{slab}^{relax} , $E_{slab}^{unrelax}$ and E_{bulk} are the energies of the relaxed slab, unrelaxed slab and the bulk crystal respectively. The n term denotes the number of bulk unit crystals in the resultant slabs. The area of the surface is denoted by the letter A . In equation (1), considering that two surfaces are produced (top and bottom) a coefficient of 2 is introduced in the denominator. The appearance of 4 in equation (2) can be explained from the fact that two surface slabs of X and Y are now considered for calculation after cleaving the bulk structure to form surface slabs. The surface energy (E_{surf}) of each of the slabs can be obtained by adding equation (1) and (2),

$$E_{surf}(X) = E_r(X) + E_c(X, Y) \quad (3)$$

The calculated surface energies are plotted in Fig. 4 for comparison. The surface slab with CuTa surface terminations results in highest surface energy of about $0.122 \text{ eV}/\text{\AA}^2$ indicating that this structure is most unstable among the slabs considered in this work. Meanwhile, CuCu surface termination is predicted to be the most stable one. Further, the figure also indicates that surface slabs with CuCu and TeTe(1) terminations are significantly more stable than CuTa and TeTe(2) surface terminations. Even though there are significant differences in the level of stability, all the free-standing surface slab models in this work are predicted to be stable since all the surface energies are positive. As already pointed out in the previous section, the outermost atomic layer in TeTe(2) surface terminations is the only surface that relaxed outward. This appears to contradict one of the important criteria of stability. This surprisingly anomalous behaviour of TeTe(2) surface slab is discussed separately in the later section.

Molecular dynamics (MD) simulation is performed for surface slab with CuCu terminations to test dynamic stability of the surface slabs for potential practical fabrication. The MD simulation is based on two classical assumptions that (i) Newton's laws of motion are obeyed by all interacting atoms and (ii) superposition theorem is satisfied [45–48]. The NVT canonical ensemble approach where the number of atoms (n), volume (V), and temperature (T) are constrained is implemented for the simulation. The energy time evolution at room temperature as predicted from the MD simulation is shown in Fig. 5. It is observed that throughout the process, energy remains almost constant with maximum energy difference of about 3 kJ/mol only. The absence of drastic energy change indicates the possible dynamical stability even at room temperature. Besides this prediction, from a practical standpoint, the application of non-equilibrium epitaxial thin film growth has been reported to be able to handle volatility of the surfaces if any exists.

3.4. Surface electronic and magnetic properties

Electronic band structure along with the corresponding DOS of the four conventional $\text{Cu}_3\text{TaTe}_4(100)$ slab models with different terminations are shown in Fig. 6. In agreement with reported literature [49], when cleaving the bulk structure and reducing the material into few atomic layers, semiconducting nature is no longer maintained. The electronic band structure of the slab models with CuCu and CuTa surface terminations exhibit half metallic (HM) behaviour with energy gap for spin down channel and metallic nature for spin up channel. Meanwhile, both the slab models with TeTe(1) and TeTe(2) terminations exhibit metallic behaviour. The HM nature exhibited by surface slabs with CuCu and CuTa terminations indicates that these materials could be suitable for spin polarized injection of charge carriers.

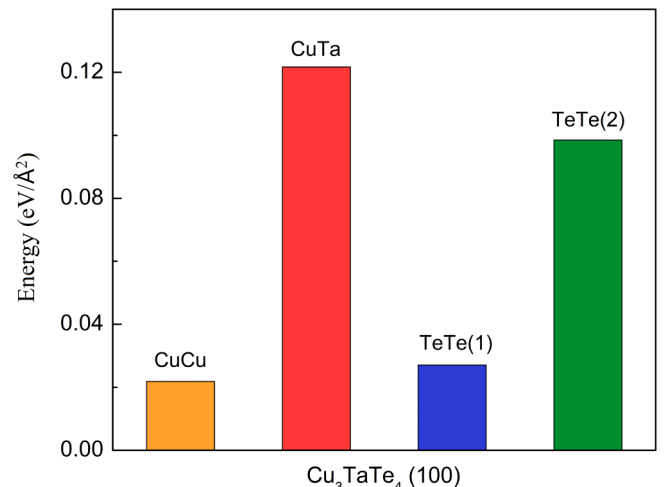


Fig. 4. Calculated E_{surf} of $\text{Cu}_3\text{TaTe}_4(100)$.

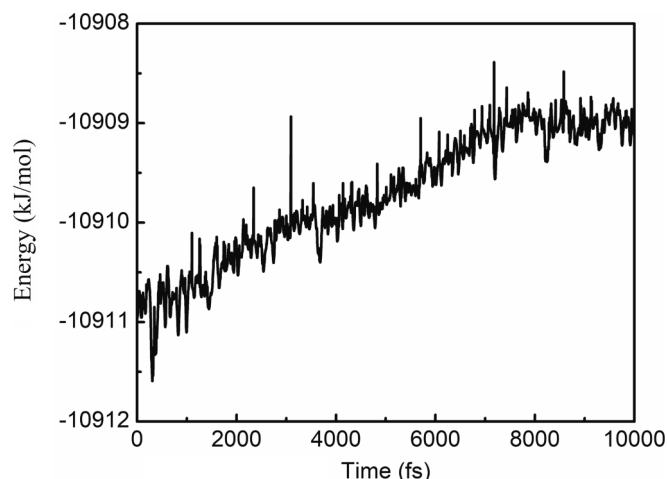


Fig. 5. Energy-time evolution of CuCu surface terminations.

Fig. 6 (b) shows that in surface slab with CuCu termination, atomic orbitals (mostly d -orbitals of Cu and Ta) from the core and σ -2 subsurface/ atomic layer are the primary contributors near the Fermi energy. Thus, the outermost atomic layer consisting of Cu atoms and the σ -2 atomic layer governs the HM property in this surface slab. Whereas, in the surface slab with CuTa termination, atomic orbitals from the outermost σ surface (mostly d -orbitals of Cu and Ta) and the adjacent

subsurface σ -1 atomic layer (mostly p -orbitals of Te) act as the major contributors for the energy states near the Fermi energy. Further, the DOS plots for the two slab models also predict that the metallic nature in these materials is mostly due to atomic orbitals from the σ surface and σ -2 subsurface (mostly d -orbitals of transition metals) crossing the E_F .

The DOS plots for surface slabs with TeTe(1) and TeTe(2) terminations are also shown in Fig. 6(b). Not only that these two surface slabs do not exhibit spin polarization, the energy states from valence band atomic orbitals clearly crosses the E_F , thus confirming fully metallic nature as seen in the electronic band structure. The DOS plots also indicate that all atomic layers (surface, subsurface, and the core region) contribute to the fully metallic nature in these two surface slabs.

It is also noteworthy that the extent by which the energy states arising from atomic orbitals crosses the E_F , is quite small in the case of surface slabs with CuCu and TeTe(1) terminations. It may be possible to transform these two systems into either p-type or n-type semiconductor through surface passivation with gas molecules. This could open another avenue for exploring the surface slabs for novel device applications.

The atomic magnetic moments and Bader charge transfer per atom of $\text{Cu}_3\text{TaTe}_4(100)$ surface (σ), and sub-surfaces (σ -1, σ -2, σ -3) of the four slab models are given in Table 2. Since, slab models with TeTe terminations do not exhibit spin polarization, they do not possess any magnetic moment and therefore, not shown in the table. Meanwhile, surface slab models with CuCu and CuTa terminations exhibit ferro-magnetic behaviour due to spin polarization of charges. The magnetic moment contributions from each atomic layer given in the table shows that Ta atoms are the main contributors. The net magnetic moment including

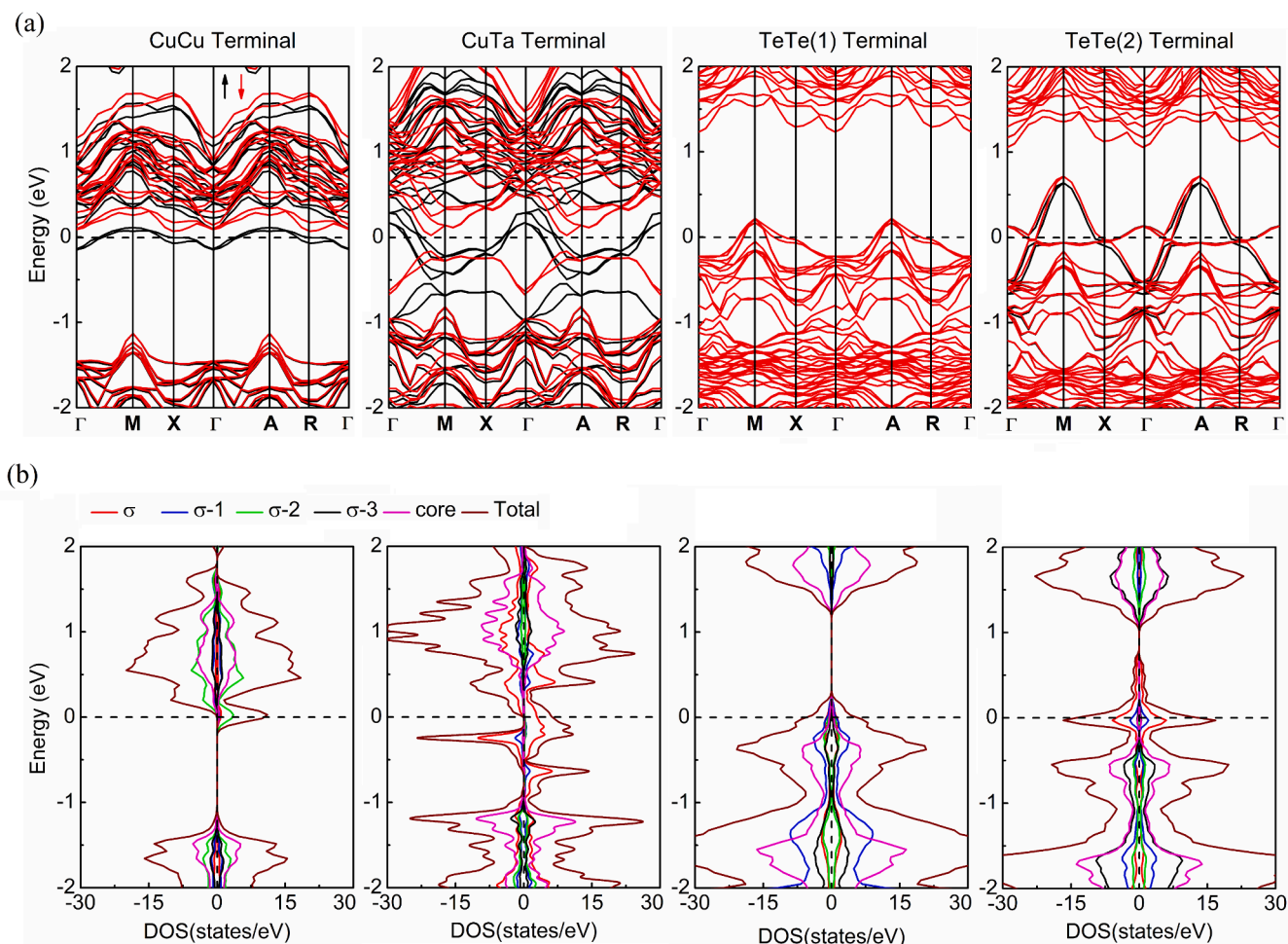


Fig. 6. (a) Electronic band structure and (b) DOS of $\text{Cu}_3\text{TaTe}_4(100)$ slab models with CuCu, CuTa, TeTe(1) and TeTe(2) terminations.

Table 2

Calculated atomic magnetic moments (in μ_B) and Bader charge transfer in the four conventional slab models of $\text{Cu}_3\text{TaTe}_4(100)$.

$\text{Cu}_3\text{TaTe}_4(100)$					
CuCu	Surface	Cu(σ)	Te(σ -1)	Cu/Ta (σ -2)	Te(σ -3)
	Magnetic moment	0.029 μ_B	0.001 μ_B	0.003 μ_B / 0.198 μ_B	-0.004 μ_B
	Bader charge	0.1038e	-0.3819e	0.0956e / 1.2249e	-0.3926e
CuTa	Surface	Cu/Ta(σ)	Te(σ -1)	Cu(σ -2)	Te(σ -3)
	Magnetic moment	0.005 μ_B / 0.696 μ_B	-0.001 μ_B	0.037 μ_B	0.004 μ_B
	Bader charge	-0.0187e / 0.7208e	-0.3339e	0.0601e	-0.3870e
TeTe (1)	Surface	Te(σ)	Cu/Ta (σ -1)	Te(σ -2)	Cu(σ -3)
	Bader charge	-0.3861e	0.1091e / 1.2594e	-0.3800e	0.0929e
TeTe (2)	Surface	Te(σ)	Cu(σ -1)	Te(σ -2)	Cu/Ta(σ -3)
	Bader charge	-0.0670e	0.1415e	-0.3570e	0.0996e / 1.2505e

contributions from the core atoms amount to 1.0 and 3.0 μ_B in surface slabs with CuCu and CuTa terminations respectively. Interestingly, the main difference in the net magnetic moment in these two systems appear to be a result of the difference in magnetic moment per atom of Ta, when it is located at the surface and at the deeper atomic layer. Magnetic moment for each Ta atom at the surface is significantly higher than when it is at the σ -2 atomic layer. This enhanced magnetic moment of surface atoms could be due to the difference in Bader charge transfer and the presence of dangling bonds at the surface [50,51]. In Table 2, the transition element Te behaves as anion and gained charges while Cu and Ta elements lose charges. However, depending on the location of ions and the termination, the charge transfer per atom varies.

3.5. Surface reconstruction of TeTe(2) terminal

The surface slab with TeTe(2) termination needs further investigation due to its outward relaxation while all the other three terminations relaxed inwards. When the bulk crystal is cleaved along (100) plane to obtain TeTe(2) termination, the other side of the cleaved surface will form CuTa termination, thus, these two surfaces are considered as surface cleavage counterpart. Out of these two surface terminations, CuTa relaxed inwards while TeTe(2) surface relaxed outwards. Therefore, CuTa surface is expected to be more stable than TeTe(2) surface. However, the surface energy calculation in section 3.3, concluded that TeTe(2) surface is relatively more stable than CuTa surface. Due to this seemingly contradicting result, we analyse the TeTe(2) and other surface terminations further. Interestingly, we found that surface recombination takes place with chemical bond formation between Te atoms in the case of TeTe(2) terminations as shown in Fig. 7, which is missing in other

surface slab models. In the figure, the structure of the surface slab considered is same as the structure displayed in Fig. 3. The only difference is that in Fig. 7 larger supercell along the plane is considered for better visual understanding. No separate DFT calculation is performed. The larger supercell shows periodic repetition along the plane so that the surface before and after relaxation can be examined to find if there are any changes.

In addition to surface visualization, further analysis is performed to ascertain the possible surface reconstruction in TeTe(2) termination. Total energy before and after relaxation are calculated for all the surface slab models. The surface slab model with TeTe(2) termination has unrelaxed total energy of -124.15 eV and after relaxation it became more stable with total energy of -127.03 eV. The difference in energy after relaxation is -2.88 eV, which is significantly larger than the corresponding energy difference in other slab models (less than -2 eV). This indicates that the relaxation process in surface slab model with TeTe(2) termination involves a certain mechanism, which effectively reduces its total energy. The possible phenomena that effectively reduces the total energy could be chemical bonding formation among Te atoms at the surface. The experimentally observed Te atomic radius is reported to be 1.23 Å [52] and our calculated distance between two Te atoms before ($d_{i\text{-Te}}^{\text{Te-Te}}$) and after ($d_{f\text{-Te}}^{\text{Te-Te}}$) relaxation at the surface (σ) are 4.356 and 2.695 Å respectively. This decrease in distance of 1.661 Å corresponds to 38.13% of the unrelaxed separation. This observation indicates that the atomic separation between Te atoms may be within the potential bond formation after structural relaxation [53–55].

The probability of discovering an electron in the vicinity space of a reference electron with the same spin and location is determined by the electron localization function (ELF) [56,57]. According to Becke and Edgecombe [58], the ELF can be expressed using the following equation:

$$n(r) = \frac{1}{1 + \chi(r)} \quad (4)$$

where $\chi(r)$ is the ratio of localization of electron $D(r)$ to uniform electron gas $D_h(r)$. This can be expressed as:

$$\chi(r) = \frac{D(r)}{D_h(r)} \quad (5)$$

Here $D(r)$ and $D_h(r)$ can be further expressed as.

$$D(r) = 0.5 \sum_{i=1}^n |\nabla \psi(r)|^2 - 0.125 \frac{|\nabla p(r)|}{p(r)} \quad (6)$$

$$D_h(r) = 0.3(3\pi^2)^{\frac{2}{3}} p(r)^{5/3} \quad (7)$$

the first term and second term in equation (6) are the kinetic energy density and the von Weizsacker kinetic energy density approximation respectively. The expression indicates that $D(r)$ is the excess kinetic energy density due to Pauli repulsion. This repulsion will be reduced in

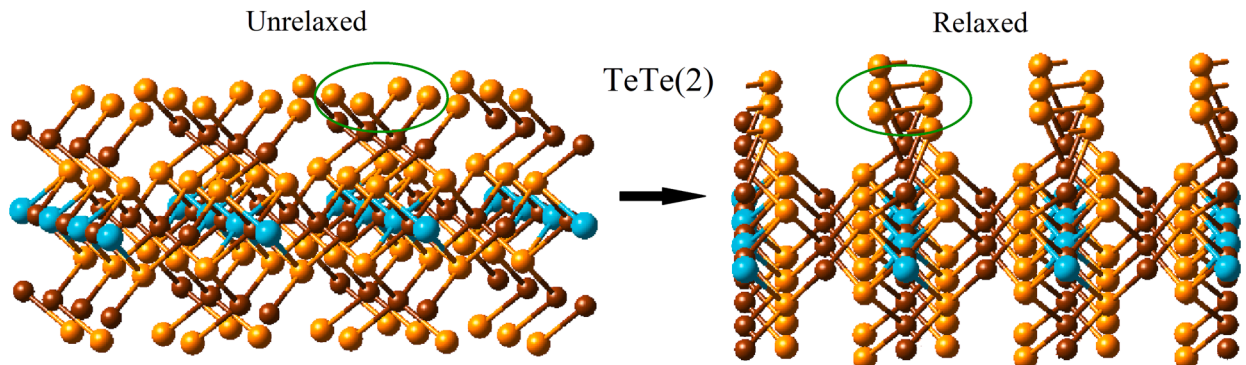


Fig. 7. TeTe(2) surface before and after relaxation.

regions where electrons are more likely to encounter lone pairs or covalent bonds rather than electrons with similar spin orientations; thus making $D(r)$ smaller in regions of high electron pair localization and vice versa. Thus in principle the ELF function will have values in the range of $0 \leq \text{ELF} \leq 1$ and will be close to unity (>0.7) for highly localised electron regions like bonding or lone pairs; while value in the range of 0.2 to 0.7 may be attributed to metallic type bonding with intermediate value 0.5 representing fully delocalised electrons [59].

Considering the theoretical knowledge as presented above, we calculate ELF for surface slab with TeTe(2) termination to make a reliable prediction in the surface recombination process. Fig. 8 shows ELF surface plot of the surface slab with TeTe(2) termination. The scale plotted in the figure corresponds to the colour coding. The red colour corresponds to high ELF value and the green colour corresponds to low ELF value or even absence of electron in the vicinity. Since, Te behaves as anion in the structure, ELF at the location of each of the Te atom is represented with red colour cloud. The two Te atoms in the inner atomic layers are clearly separated. However, the two Te atoms at the surface

(top of the structure in the figure) are joined with slightly reddish thin yellow colour. From the colour coding, the ELF value corresponding to this colour can be interpreted as somewhere between 0.5 and 0.7. This indicates the presence of delocalized electrons presumably metallic bonding between the two Te atoms. At the bottom most atomic positions, a solid circle appears indicating the same Te-Te chemical bonding. This seemingly variation in graphical representation is due to the alignment of Te-Te atoms. The alignment is such that the orientation is along the contour plane at the top most position while it is perpendicular to the plane at the bottom most atomic position. Since, the ELF corresponding to Te atoms within the inner atomic layers are clearly separated, it shows that there is no chemical bonding between them. These observations lead to our conclusion that surface recombination process indeed occurs in surface slab with TeTe(2) terminations and is thus relatively more stable than its surface counterparts, the surface slab with CuTa termination.

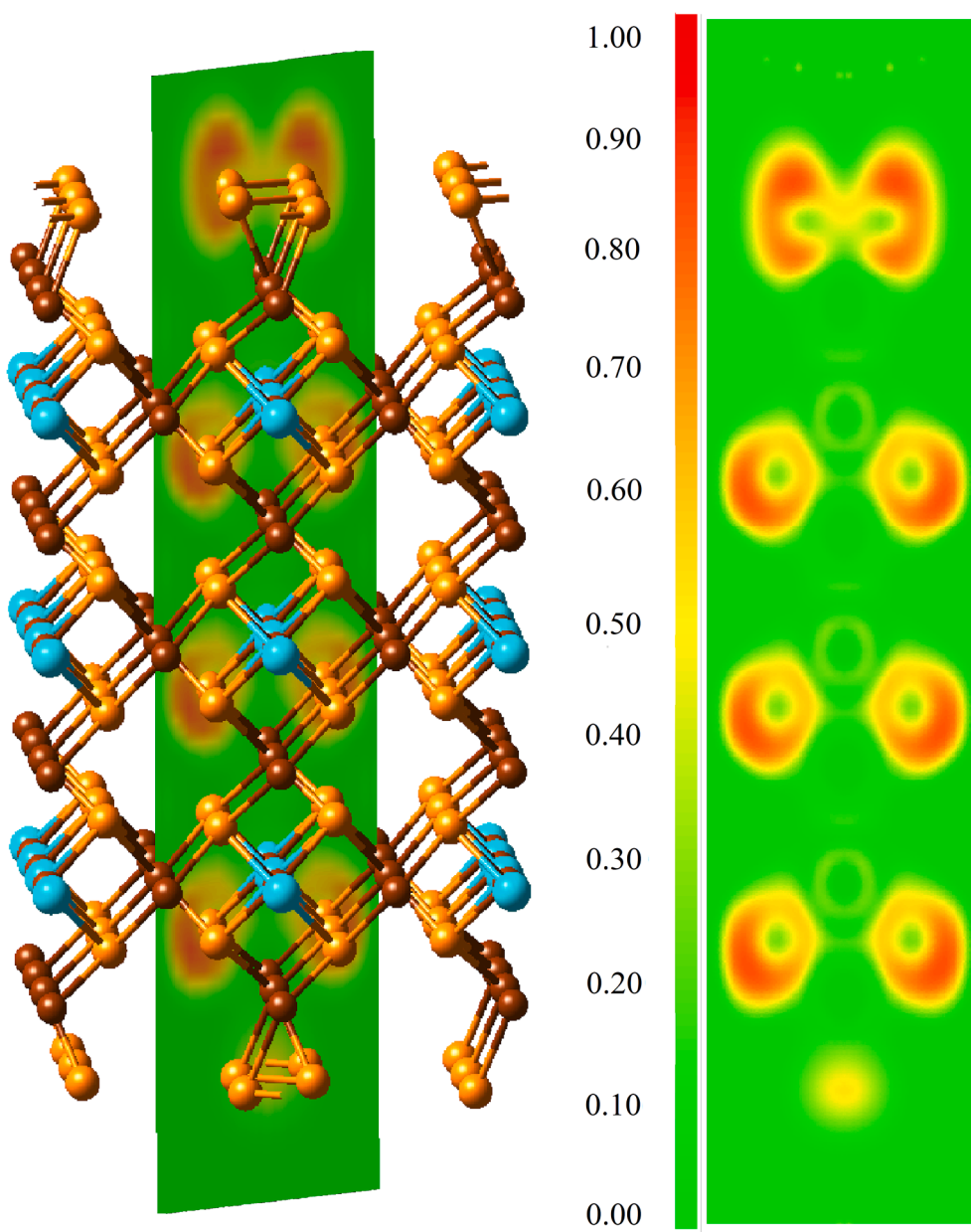


Fig. 8. ELF surface plot of TeTe(2) terminal.

4. Conclusion

In summary, we explore the (100) surface properties of Cu_3TaTe_4 sylvanite compound within the framework of spin-polarized DFT calculations. To validate our findings and to understand the changes that occur when choosing thin layer of Cu_3TaTe_4 compound, DFT calculations was first performed on the bulk structure. Structural and electronic properties obtained are in good agreement with reported literature. The bulk structure was cleaved along (100) crystal plane such that four possible symmetric terminations with CuCu, CuTa, TeTe(1), and TeTe(2) atoms at the surface are obtained. Surface energy calculation predicts that surface slab with CuCu termination is most stable and CuTa termination is most unstable. Meanwhile, the structural parameters after relaxation indicate that TeTe(2) surface could be most unstable due to its outward relaxation. ELF calculations have shown that this seemingly contradicting results could be due to surface reconstruction in TeTe(2) surface, which significantly lowers the energy of the system. Electronic band structures of Cu_3TaTe_4 (100) surface slabs exhibit transition from semiconducting nature in bulk crystal to either half metallic or fully metallic nature depending on the termination. The HM nature in CuCu and CuTa surface terminations provide promising theoretical data for future development of spintronic device. Further, surface slabs with CuCu and CuTa terminations have been found to possess desirable net magnetic moment of 1.0 and 3.0 μ_B respectively for the said device applications.

CRediT authorship contribution statement

Bernard Lalroliana: Conceptualization, Writing – original draft, Software, Investigation, Formal analysis, Visualization. **Lalmuanchhana:** Writing – review & editing, Investigation, Formal analysis. **Lalhumhima:** Writing – review & editing, Formal analysis. **Lalrinkima:** Writing – review & editing. **Shivraj Gurung:** Conceptualization, Resources. **Y. Rangeela Devi:** Writing – review & editing. **Ningthoujam Surajkumar Singh:** Writing – review & editing. **Zodinmawia:** Conceptualization, Resources. **Dibya Prakash Rai:** Writing – review & editing, Conceptualization, Formal analysis. **Lalhriatzuala:** Conceptualization, Methodology, Writing – review & editing, Resources, Supervision, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Research Papers

Nb-based copper sylvanites for potential green energy harvesting under induced isotropic pressure

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ABSTRACT

This work explores the mechanical, electronic, dynamical stability, optical, and thermoelectric properties of Nb-based copper sylvanite compounds Cu_3NbX_4 (X=S, Se, Te) at 0, 5, 10, 15, and 20 GPa isotropic pressure within the framework of density functional theory (DFT). Calculated results are found in good agreement with experimental data, specifically in the values of their lattice parameters and optical band gaps. Cu_3NbX_4 exhibits promising optical properties for photovoltaic applications with enhanced properties under pressure. Exploration on transport properties also shows moderate thermoelectric figure of merit with slight improvement under pressure.

1. Introduction

The availability and ease of access to energy have been one of the driving factors for development of mankind. The rapid growth in population along with technological advancements has led to further supplementary energy demands. The population growth is expected to increase continuously and thus energy demands are also projected to rise in folds. This upsurge in energy demands has ultimately led to the growth of energy production as well as consumption; which at present is met chiefly from non-renewable energy sources commonly fossil fuels. Though fossil fuels play a significant role in the energy sector, they are prone to exhaustion. Moreover, such energy sources have an adverse effect on the environment through the discharge of toxic residues. Therefore, it is imperative to explore novel energy sources and energy harvesting means, that satisfy the growing demands while simultaneously eliminating or minimizing the adverse effects on the environment. This motivation has led researchers to approach green energy that might be met through renewable sources.

The sun is a boundless source of energy, with the earth receiving about $1.366 \times 10^3 \text{ Wm}^{-2}$ of solar constant [1], thus it is worthwhile to look for means to harness this energy. This study will initially emphasize on the prospects of the copper sylvanite compounds as light absorbers for solar photovoltaics (PV's) applications. Further, one of the by-products of widespread use of machines in this modern age, is the

dissipation of energy in the form of waste heat. At the global scale, useful work done by the utilization of heat is estimated to be only 20 %, implying that an astonishing 80 % of the total energy is being lost in the form of heat, which directly contributes to global warming [2]. Therefore, it is apparent that harnessing this unused energy could assist in fulfilling global energy demands while simultaneously minimizing the global warming effect. Thus, the study will also explore the compounds on prospects of their thermoelectric (TE) viability, which converts waste heat directly to electricity without the requirement of any mechanical moving parts.

Theoretically, the prospects of copper sylvanite compounds (CSCs) for solar PV's as well as TE materials have already been studied extensively [3–12]. Studies have revealed that these groups of compounds exhibit promising properties because their band gaps lie close to the optimum value of $\sim 1.5 \text{ eV}$ for PV's [13,14]. At ambient pressure, Kehoe et al., [9,15] extensively explored the same within the GGA formalism and hybrid functionals and effective Hubbard correction (U) of 5.2 eV in Cu-d orbitals. For Nb-based compounds, the authors reported that implementing U correction approximates band gaps closer to experimental values than hybrid functionals like HSE06. Further, Espinosa-García, W.F. et al., [13] reported similar optical band gaps (OBG) for similar functionals. Hersh P.A. [16] and Chen et al., [17] independently measured the experimental OBG of Cu_3NbS_4 and Cu_3NbSe_4 as 2.56, 2.13 eV and 2.6, 2.2 eV respectively, while experimental measurements for

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Cu_3NbTe_4 is yet to be achieved. The potency for TE materials can be understood from the dimensionless figure of merit $ZT = \frac{S^2\sigma}{\kappa_T}T$, where the product $S^2\sigma$ is power factor (PF), T the absolute temperature, and κ_T ($\kappa_T = \kappa_e + \kappa_l$) the total thermal conductivity. For high TE performance, it is ideal to have high PF and a low total sum of the electronic part of thermal conductivity (κ_e) and lattice thermal conductivity (κ_l). Enhancing PF is quite a challenge to researchers since its constituent terms are coupled, and enhancement in one term tends to effectively subdue the other and vice versa. Thus, techniques on minimizing κ_T to improve ZT has been an interesting area for researchers. CSCs for potential TE materials has been reported in several literatures [7,8,17,18]. In theory, Nb-based CSCs are predicted to have high ZT > 1 at higher temperatures, suggesting high TE performance. Assertions are also made where in the enhanced ZT arrives not only from their high PF but also due to low κ_l . Thus, so far as theory is concerned, CSCs exhibit promising properties for potential light absorbers as well as good TE materials.

Theoretically, CSCs have been widely explored regarding their PV's as well as TE applications under ambient conditions. Various reports using different functionals outline diverse OBG, which sometimes deviates extensively from experimental values [13,19]. Accurate determination of OBG from electronic properties is of utmost importance, as prediction of compound for PV's and TE materials primarily depends on it. With regards to OBG for CSCs, it is already discussed in literature that applying $U = 5.2$ eV to *Cu-d* orbitals predicts OBG values comparable to experimental measurements while GGA underestimate and hybrid functionals overestimate [9,13,15]. The U value in this literature has not been explicitly calculated but rather incorporated directly from reported literature on different compounds. Also, perhaps for the same reason, authors have failed to implement U correction for the other transition metal-Nb. Further, U tends to reorganize electronic dispersion curves and thus, apart from determining the band gap, it can predict diverse electronic properties. Moreover, when semiempirical method is used for U prediction instead of *ab initio* approach, capturing modifications in on-site interaction under physical changes due to variations in chemical reactions etc., cannot be realized [20]. Therefore, it is presumable that there is still room for the prediction of properties using *ab initio* U approach. One of the straightforward means to perturb crystals in DFT is straining the crystal, which can be brought about by inducing pressure. Pressure, in principle can lead to the reconstruction of electronic dispersion curves resulting in band gap modifications, direct/indirect electronic band transitions, etc. It would also be outstanding if high pressure induces a negative pressure coefficient on the fundamental band gaps so that relatively lower energies of the solar spectrum could now interact, which otherwise are wholly discarded due to band gaps. Further, narrowing band gaps through perturbation could improve ZT by enhancing σ while effectively lowering κ_l [21–23]. Moreover, experimental results suggest that pressure could enhance TE performance and improve TE efficiency by a factor of ~10–40 in *p*- Bi_2Te_3 [24] where pressure is brought about in anvil cells in the Bridgman type and that of toroidal shape. Su, N. et al., [25] reported PF improvement in SnSe by three folds at 22 kbar pressure by the clamp-type piston-cylinder cell method, while general trends on such properties for various materials and approaches can be found in Ref. [26]. Based on the above facts and understandings, this work primarily investigates the optical and electron transport properties under pressure by applying *ab initio* U correction as well as spin-orbit coupling (SOC) for additional accurate predictions.

2. Computational details

First principle calculations were carried out using the generalized gradient approximation (GGA) based on the projector augmented wave (PAW) [27–30] method using MedeA-VASP 5.4 (Vienna Ab Initio Simulation Package) [31–33] code. For self-consistent field (SCF) calculations, a dense $8 \times 8 \times 8$ k-mesh was used according to

Monkhorst-Pack [34] scheme. A planewave cut-off energy of 400 eV was used, and atoms were relaxed until the forces between adjacent atoms were smaller than 0.01 eV/Å. Electronic convergence criteria of 10^{-6} eV and the Normal block Davidson method with linear tetrahedron method (with Bloechl correction) [35] were employed. For electronic property calculations, a denser k-mesh of $12 \times 12 \times 12$ was used for more accurate calculations with the incorporation of U simultaneously with SOC. The compounds were perturbed by applying compressive isotropic pressures up to 20 GPa in steps of 5 GPa. Dynamical stability under such pressures was tested from phonon calculations for which $10 \times 10 \times 10$ k-mesh and cut-off energy increased to 520 eV for more accuracy. Mechanical properties and mechanical stability were calculated using *ab initio* approach as developed by Le Page, Y. and P. Saxe [36,37].

The on-site Coulomb interactions of Dudarev's rotationally invariant DFT+ U [38] *ab initio* approach were employed as implemented in Quantum Espresso (QE) code [39,40] which is also PAW potential-based. The application of pressure in the order of GPa, alters the lattice parameters of Cu_3NbX_4 significantly, which effectively modifies the electronic properties. For a better understanding of this variation, this study computes the effective U at each pressure. The pressure-dependent U is presented in Table 1. The primary purpose of the U correction is to consider the strong on-site Coulomb interaction of localized electrons with the Hubbard-like term. The Hubbard Hamiltonian describes the strongly correlated electronic states mainly in the *d* and *f* orbitals, while the rest of the valence electrons are treated using the usual DFT approximations. In general, this implies that more the number of electrons in *d* orbitals, the more will be Coulombic repulsion; resulting in larger U correction values. Consequently, Cu consisting of more *d*-electrons in its valence shell than Nb exhibits higher U values. Moreover, as U values fall within the same range at all pressures, we can assume dependence on U due to pressure is minimal for our CSCs.

For transport property calculations, the DFT post processing tool of semiclassical Boltzmann transport equations integrated into MedeA-VASP 5.4 BoltzTraP code is employed. The wavefunctions were recalculated at k-mesh of $30 \times 30 \times 30$ in the first Brillouin zone. Furthermore, the default constant relaxation time approximation (CRTA) $\tau=10^{-14}$ s as well as relaxation time approximation (RTA) as obtained from deformation potential theory are assumed for investigation of the transport properties.

3. Results and discussion

3.1. Structural and mechanical properties

The crystal structure of CSC is as shown in Fig. 1. The compounds are cubic with P-43m space symmetry group, and the asymmetric unit of the crystal structure is comprised of three Cu, one Nb, and four X (= S, Se, Te) atoms. Nb atom is located at the eight corners of the cell in Wyckoff's position 1a (0,0,0); Cu atoms at 3d (0.5,0,0) and X (= S, Se, Te) atoms situated at 4e (x,x,x). Table 2 presents the calculated lattice parameters at different pressures, which is consistent with other theoretical and experimental data [41–46]. As expected, the lattice parameter increases down the chalcogenide groups.

Our results indicate that the compounds maintain cubic phases on application of isotropic compressive pressure along the three axes of the

Table 1
Ab initio predicted U (in eV) for d-orbitals.

Cu_3NbX_4	Atomic-d orbitals for U	0 GPa	5 GPa	10 GPa	15 GPa	20 GPa
Cu_3NbS_4	Cu	11.28	11.34	11.35	11.35	11.35
	Nb	3.10	3.12	3.13	3.14	3.14
Cu_3NbSe_4	Cu	11.06	11.04	11.06	11.07	11.08
	Nb	3.19	3.19	3.19	3.19	3.19
Cu_3NbTe_4	Cu	11.22	11.29	11.33	11.39	11.47
	Nb	3.17	3.20	3.20	3.20	3.20

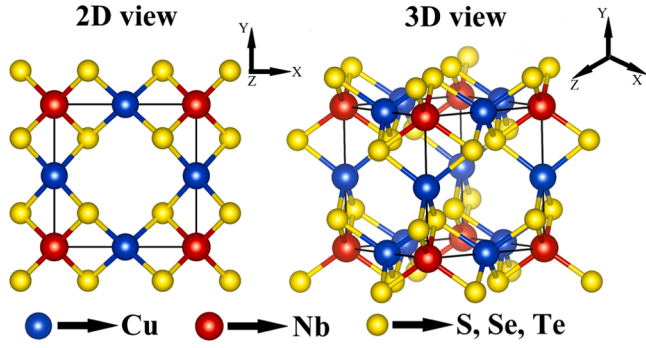


Fig. 1. Crystal structure of Cu_3NbX_4 ($\text{X}=\text{S}, \text{Se}$ and Te).

asymmetric crystal structure, even though deformations can trigger structural phase transitions in particular compounds [47–51]. This implies that under the pressure limit, stress/strain causes uniform equivalent changes in all axes. To verify the dynamical stability [52] of CSCs at these pressures, phonon calculations were performed, and resultant dispersion curves are presented in Fig.S5. The absence of negative frequencies in the pressure limit confirms the dynamical stabilities of the compounds at least up to 20 GPa.

To determine if a compound satisfies the necessary requirements for practical synthesis; stability, durability, brittleness, etc., analysis from the elastic constant plays a crucial role [53]. In light of this, we examine the elastic constants for mechanical stability according to Mouhat et al., [54]. The various elastic constants of cubic crystals may be defined by three distinct elastic parameters only: C_{11} , C_{12} , and C_{44} . Predicted elastic constants and hence various elastic moduli are in close agreement with theoretical values for similar exchange-correlation function [3,8,55]. The cubic nature of the CSC structures is re-confirmed from these elastic constants as C_{14} , C_{42} , C_{24} , and C_{34} etc., all vanishes. The following is how the Born requirements for mechanical stability are determined [56]:

$$C_{11} - C_{12} > 0; C_{11} + 2C_{12} > 0; C_{44} > 0 \quad (1)$$

Under the influence of pressure, Eq. (1) can be modified according to Sin'ko et al. [57] as

$$\tilde{C}_{11} > 0, \tilde{C}_{11} > |\tilde{C}_{12}|, \tilde{C}_{44} > 0, \tilde{C}_{11} + 2\tilde{C}_{12} > 0 \quad (2)$$

where

$$\tilde{C}_{11} = C_{11} - P, \tilde{C}_{12} = C_{12} + P, \tilde{C}_{44} = C_{44} - P, (P \rightarrow \text{applied pressure}) \quad (3)$$

The Hill's approximation to mechanical properties from elastic constants can be derived from prior knowledge of Voigt [60] (subscript V) and Reuss [61] (subscript R) assumption as follows:

$$B_R = B_V = \frac{(2C_{12} + C_{11})}{3} \quad (4)$$

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3C_{11} - 3C_{12}}, \text{ and } G_V = \frac{(3C_{44} + C_{11} - C_{12})}{5} \quad (5)$$

From Eqs. (4)–(5), elastic properties within Hill's assumption can be derived following the formula

$$B = \frac{B_V + B_R}{2} \quad (6)$$

$$G = \frac{G_V + G_R}{2} \quad (7)$$

Subsequently, Y and ν can be calculated,

$$Y = \frac{9GB}{3B + G} \quad (8)$$

$$\nu = \frac{3B - 2G}{2(G + 3B)} \quad (9)$$

The Grüneisen parameter can then be derived from ν using the formula

$$\gamma = \frac{3}{2} \left(\frac{\nu + 1}{2 - 3\nu} \right) \quad (10)$$

Table 2 clearly highlights that elastic constants satisfy all necessary and sufficient conditions for mechanical stability indicating their stability towards elastic deformations. Based on the elastic constants (C_{11} , C_{12} , C_{44}), analysis of different elastic moduli was carried out by making use of Hill equations [62–64]. The mechanical property of a solid can be defined by its elastic moduli. In the domains of engineering and crystal physics, the resistance to fracture may be deduced from the bulk modulus (B); the greater the value, the greater the resistance to fracture. Furthermore, the shear modulus (G) can be used to infer resistance to plastic deformation. According to our estimates, under large compressive stresses, the B value dramatically rises according to Eq. 4 as C_{11} and C_{21} drastically escalate. Similar conclusions, however, cannot be drawn in G as all the three independent parameters of C_{11} , C_{12} , and C_{44} are correlated into Eq. (5). All this result suggests that CSC crystals will not fracture or deform plastically at high compressive pressure. Eq. (8) gives the ratio of stress to strain, or Young's modulus (Y), that indicates the stiffness of a material, which also tends to increase with pressure for our compounds. Poisson's ratio (ν) according to Eq. (9), and Pugh's ratio (B/G) [65] were deduced from the elastic moduli. ν provides the essential details about the type of bonding that occurs in crystals, whether it is metallic or covalent. Bonding is regarded as metallic when $\nu > 0.33$, but covalent when ν is around ~ 0.1 [66]. Findings indicate

Table 2

represents the Lattice parameter a (Å); elastic constants C_{11} , C_{12} and C_{44} (GPa); Bulk modulus B , Shear modulus G , and Young's modulus Y (GPa); dimensionless Poisson's ratio ν , Pugh's ratio B/G ; and Debye temperature Θ_D (Kelvin) for CSC at 0, 5, 10, 15 and 20 GPa isotropic pressure.

Cu_3NbX_4	GPa	a	C_{11}	C_{12}	C_{44}	B	G	Y	ν	B/G	γ [58]	θ_D [59]
Cu_3NbS_4	0	5.54	93.08	10.11	28.05	37.77	32.83	76.35	0.16	1.15	1.1547	337.5
	5	5.35	126.64	25.74	29.85	59.38	36.88	91.65	0.24	1.61	1.4655	359.7
	10	5.22	158.12	40.79	31.57	79.90	40.57	104.06	0.28	1.97	1.6714	377.0
	15	5.13	184.66	54.32	25.20	97.77	37.29	99.15	0.33	2.62	1.9811	361.9
	20	5.05	211.26	69.76	26.68	116.92	39.92	107.40	0.35	2.93	2.1047	373.3
Cu_3NbSe_4	0	5.72	79.23	15.34	25.47	36.63	27.89	66.74	0.20	1.31	1.2720	263.0
	5	5.51	117.51	39.44	29.18	65.46	32.79	84.29	0.28	2.00	1.6857	286.3
	10	5.37	143.87	54.64	27.51	84.38	33.42	88.56	0.33	2.52	1.9395	288.8
	15	5.26	174.35	72.80	31.88	106.65	38.45	102.96	0.34	2.77	2.0439	308.4
	20	5.18	199.10	87.82	35.63	124.92	42.63	114.81	0.35	2.93	2.1053	323.5
Cu_3NbTe_4	0	6.00	62.27	16.54	32.34	31.79	28.15	65.19	0.16	1.13	1.1388	234.2
	5	5.76	91.65	34.13	30.82	53.30	29.98	75.73	0.26	1.78	1.5655	243.3
	10	5.61	122.86	56.15	38.09	78.39	36.12	93.93	0.30	2.17	1.7744	266.3
	15	5.51	154.44	80.23	43.31	104.97	40.71	108.16	0.33	2.58	1.9626	281.8
	20	5.43	177.69	97.03	46.47	123.92	43.91	117.81	0.34	2.82	2.0631	291.8

that the ν increases as pressure rises, signifying a lesser covalent bonding nature. At 20 GPa, the ν even surpasses 0.33, indicating a partial metallic-like transition of the chemical bond.

Pugh's ratio criteria [65] states that a compound is brittle if its B/G ratio is less than 1.75 and ductile otherwise. The three CSCs under investigation have their respective ratios less than 1.75, indicating that they are brittle, which is consistent with existing literature [7,41]. However, as pressure is induced, this ratio begins to rise linearly and increases beyond 1.75 after a certain pressure relative to the compound. Also, for predicting melting temperatures (T_m) of the compounds, the expression $T_m = 553 + 5.91C_{11}$ was implemented according to Fine et al., [67] and is obtained to be 901K, 1001K, and 1083K, respectively, for $X = \text{Te}$, Se , and S . The relationship between strain and pressure is shown in Fig. 2. It is observed that all three CSCs exhibit almost similar strain under the same isotropic pressure. At 20 GPa, pressure induces around 9 % maximum strain on all the compounds. However, when strictly speaking, Cu_3NbS_4 exhibits a minimum strain-to-pressure ratio, followed by Cu_3NbSe_4 and Cu_3NbTe_4 , indicating difficulty to volume change. This idea can also be inferred from their Bulk modulus 'B' value, which mainly depends on C_{11} in their pristine states (at 0 GPa) where B indicates resistance towards volume change due to external deformations. Consequently, Cu_3NbS_4 possessing a comparatively higher B value displays minimum strain due to pressure, followed by Cu_3NbSe_4 and Cu_3NbTe_4 as expected.

3.2. Electronic properties

Estimation of band gaps comparable to experimental values is one of the main emphases and challenges in DFT. Especially for semiconductors, the band gap largely aids in speculating applicability for certain applications and device fabrication, etc. Further, for this study, where the focus is on optoelectronic and TE applications, band gaps play a crucial role because, beyond certain limits, the compounds could be rendered less efficient or completely impractical for such applications. From discussions in the supplementary part, it is observed that GGA formalism underestimates the band gaps while GGA+U predicts comparable results to experimental data. Thus, for electronic property calculations, we proceed with this study for higher pressures with U correction only. However, to grasp any relativistic effect on the compounds, SOC is also simultaneously employed.

The electronic band structures along R-X- Γ -M-R- Γ high symmetry points with corresponding partial density of states (PDOS) calculated using GGA+U+SOC for the investigated compounds at 0 and 20 GPa are presented in Fig. 3 and the intermediate pressures 5–15 GPa are illustrated in Fig.S2. The variation of energy band gaps with pressure is

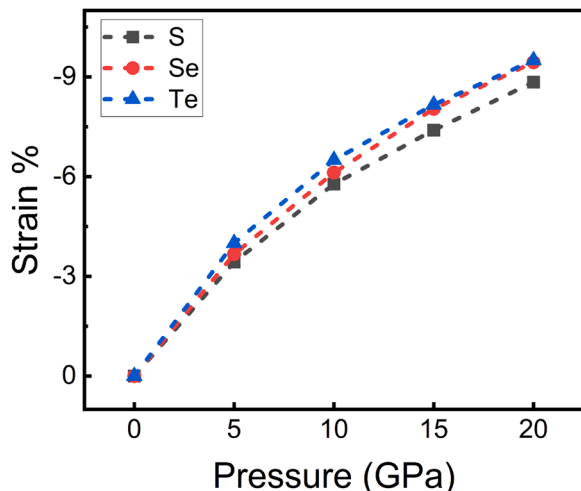


Fig. 2. Strain vs Pressure for Cu_3NbX_4 .

presented in Table 3. From the result, it can be concluded that CSCs are indirect band gap semiconductors with decreasing energy band gaps down the chalcogenide groups, which is consistent with literature from theory as well as experiments [14]. The valence band maximum (VBM) and conduction band minimum (CBM) are located at the R and X symmetry points of the first Brillouin zone respectively. It is also observed that the effect of SOC increases down the chalcogenide groups, which is appreciable due to the introduction of successively heavier atoms. Almost no significant band splitting occurs in Cu_3NbS_4 while maximum splitting is observed for the heaviest Cu_3NbTe_4 compound, with an intermediate effect occurring for Cu_3NbSe_4 . Furthermore, band splitting due to SOC occurs along the high symmetry point R with split-off energy in the order $\text{Cu}_3\text{NbS}_4 < \text{Cu}_3\text{NbSe}_4 < \text{Cu}_3\text{NbTe}_4$; whereas split-off energy is completely absent in the sulphur base CSC.

From PDOS analysis, d-orbitals of Nb persist as the main contributor to the conduction band (CB) near the Fermi level E_F ($= 0$ eV) with minor contributions from possible hybridized states of X-p and Cu-d orbitals. In the valence band (VB) all possible hybridized states from p-orbitals of chalcogenide atoms, Nb-d and Cu-d orbitals contribute near the E_F while Cu-d orbitals persist to be the dominant contributor in the deeper energy bands (~ -4 eV).

Upon inducing pressure, the fundamental band gap decreases congruently wherein for Cu_3NbS_4 , Cu_3NbSe_4 , and Cu_3NbTe_4 the gaps fall in the range 2.23–1.67 eV, 1.72–0.99 eV, and 1.02–0.22 eV respectively. This diminishing band gap with pressure suggests enhanced optoelectronics as well as TE properties, consequently lower energy ranges can be utilized beneficially which was otherwise directly excluded when the compound possesses larger energy band gaps at ambient pressure. The narrowing of band gaps is due to the modification in the dispersion curves, which results in energy bands from the CB pushed towards the E_F . The orbital contributors to energy bands under pressure are identical to 0 GPa with a narrowing of the gap between the VB and CB in congruence with the electronic dispersion bands.

3.3. Optical properties

The examination of optical characteristics helps to understand how materials interact with incident radiation. The obtained optical characteristics using DFT+U+SOC of the CSCs are isotropic along the three axes due to their cubic structure. The real (η) and imaginary (k) parts of the refractive index (also known as the extinction coefficient), and the absorption coefficient (α), among other significant optical characteristics, may be obtained from the complex dielectric function (ϵ), which has two parts: the real (ϵ_1) and imaginary (ϵ_2). It can be revealed that the complex dielectric function directly correlates with electronic properties and its expression is as follows [68]:

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \quad (11)$$

$\epsilon_2(\omega)$ maybe directly obtained from the occupied and unoccupied wave functions of the momentum matrix which reflects mostly the indirect observables of the complex dielectric function, such as absorption, dielectric loss, energy loss, etc.

$$\epsilon_2(\omega) = \frac{h^2 e^2}{\pi m^2 \omega^2} \sum_m \int d^3k \left| \vec{k} n \right| \vec{p} \left| \vec{k} n' \right|^2 x \left[1 - f(\vec{k} n) \delta(E_{\vec{k} n} - E_{\vec{k} n'} - \hbar\omega) \right] \quad (12)$$

Using the well-known Kramers-Kronig transformation, one may extract the real part of the dielectric function $\epsilon_1(\omega)$, which represents the polarizability of materials with incoming radiation without absorbing energy [69]:

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (13)$$

Resultant plots for $\epsilon(\omega)$ at 0, 5, 10, 15 and 20 GPa for Cu_3NbX_4 ($X =$

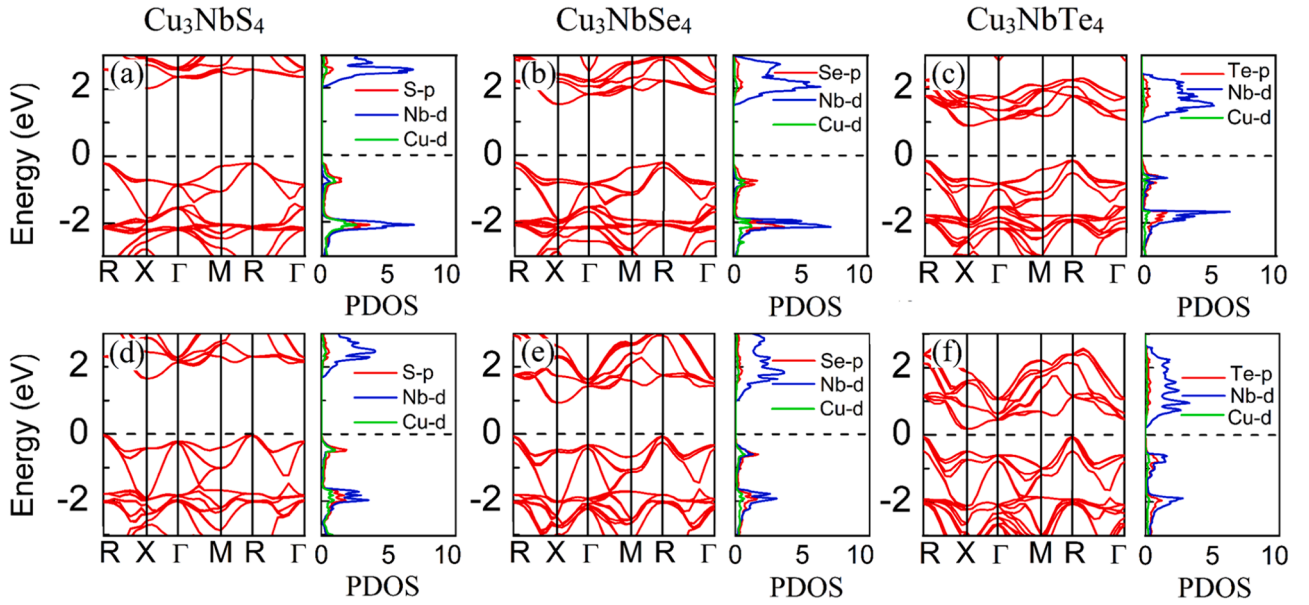


Fig. 3. Calculated electronic band structures of Cu_3NbX_4 ($X=\text{S, Se, Te}$) using DFT+U+SOC at 0 GPa (a–c) and 20 GPa (d–f).

Table 3

Variation of energy band gaps (eV) with pressure for Cu_3NbX_4 ($X=\text{S, Se and Te}$).

Cu_3NbX_4	0 GPa	5 GPa	10 GPa	15 GPa	20 GPa
Cu_3NbS_4	2.23, 1.65 [41], 2.66 [13], 1.82 [9]	2.08	1.94	1.81	1.67
Cu_3NbSe_4	1.72, 2.20 [13], 1.45 [9]	1.50	1.31	1.14	0.99
Cu_3NbTe_4	1.02, 0.92 [9], 1.62 [9]	0.74	0.52	0.35	0.22

S, Se, Te) are presented in Fig. 4. It can be generalised that optical activity increases down the chalcogenide groups for CSCs. Interestingly, a significant portion of optical activity falls within the visible range which is ideal for PV applications. At ambient pressure, static dielectric constants $\epsilon_1(0)$ are 6.5, 7.5, and 10.2 respectively for CSC down the chalcogenide groups; which gradually increases with the energy of incident radiation, reached the first peak in the visible range and then decreases again. This high $\epsilon_1(0)$ is quite desirable for solar PV's as materials with such properties tend to decrease charge carrier recombination rates. Negative $\epsilon_1(\omega)$ observed in certain photon energy ranges indicates metallic reflectivity in that region disclosing additional potential applications in wave absorbing, wave transmission in antennas, and electromagnetic radiation shields, etc [70,71]. From the plot of $\epsilon_2(\omega)$, it can be seen that optical activity ceases to exist until certain incident radiation. Optical activity edge (OAE), which can be defined as

the onset when $\epsilon_2(\omega) > 0$, is in general maximum in S-based CSCs, decreases for Se and the least for Te compounds. On the onset of OAE, $\epsilon_2(\omega)$ rapidly increases some falling in the visible range, especially for Te-CSCs suggesting potential optoelectronics application. When pressure is induced optical properties are enhanced especially in the IR-vis range. $\epsilon_1(\omega)$ subsequently increases for the three compounds until certain energy region and red shifting in their respective peaks. Due to the same, the onset of metallic reflectivity is red-shifted particularly for Cu_3NbTe_4 , reflection could occur at around ~ 3.0 eV signifying their effectiveness as blue-UV light reflectors. The same pressure also correspondingly causes imaginary part $\epsilon_2(\omega)$ of dielectric function to red shift in their optical peaks as well as in their OAE. This once more suggests stronger activity (perhaps absorption, etc.) in the visible energy spectrum, pointing towards prospects for potential solar PV's. To validate such claims, further insight into complex refractive index and optical absorption were explored.

Perhaps the most important optical constant for PV's material as an absorbing medium is the complex refractive index. The function comprises of two parts: the imaginary part, known as the extinction coefficient or loss function (k) which describes the loss of photon energy during propagation through the optical medium, and the real part, or refractive index (n) which indirectly determines how fast or slow, photon travels in a medium with respect to vacuum. The relation of these functions with dielectric function is given below [72]:

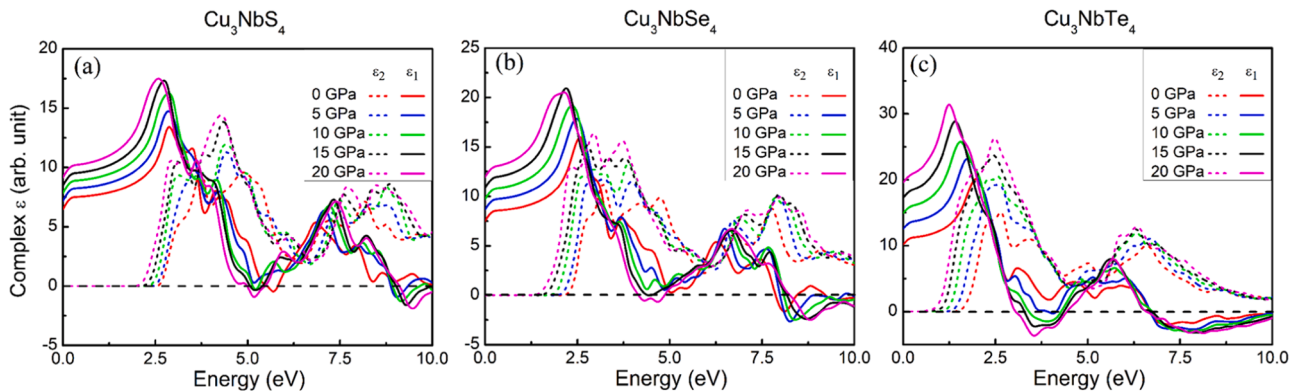


Fig. 4. Predicted $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ for Cu_3NbX_4 ($X = \text{S, Se, Te}$) using DFT+U+SOC.

$$\eta(\omega) = \frac{1}{\sqrt{2}} \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{1/2} \quad (14)$$

$$k(\omega) = \frac{1}{\sqrt{2}} \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega) \right]^{1/2} \quad (15)$$

For the three compounds, concerning change in photon energy, η increases and reaches its maximum value at ~ 2.89 – 2.07 eV down the chalcogenide groups, after which it abruptly falls once again. Normal dispersion is elucidated by the rise in η with increasing incident energy, whereas anomalous dispersion is indicated by a drop in η with rising energy. Since anomalous dispersion frequently happens in areas with high radiation absorption, it is of distinct importance for this study. The k is maintained at zero up to a certain energy range with sudden optical activity at ~ 1.68 – 2.68 eV, indicating the onset of energy-related interaction from that range. The absorption coefficient (α) can be better for interpreting the loss of photon energy during media propagation, the functional change of k is thus correlated with α and will be covered in the next section. With pressures of 5, 10, 15, and 20 GPa, η not only amplify with photon energy but also redshift in its peak position. This indicates applying pressure can cause the onset of anomalous dispersion to shift to lower photon energy directing enhanced radiation absorption towards the visible range. It can be noted that η and k curves overlap for the same energy range as $\varepsilon_1(\omega) < 0$ depicting the same total reflection in the region as shown in Fig. 5.

The ' α ' and ' k ' relation can be expressed as [73]:

$$\alpha(\omega) = \frac{4\pi k(\omega)}{\lambda} \quad (16)$$

The plot of α against incident photon energy is shown in Fig. 6. Since most solar PV's operate in the IR-vis-UV spectrum upper energy limit of up to 5 eV is considered. For Cu_3NbS_4 , Cu_3NbSe_4 , and Cu_3NbTe_4 , the absorption edge occurs at 2.69, 2.34 and 1.84 eV respectively at 0 GPa. This is above the energy band gap determined from electronic band structures, indicating that the compounds are indeed indirect band gap semiconductors. Even under ambient pressure, CSCs exhibit good optical absorption in the order of 10^5 cm^{-1} throughout the photon energy range. Prominent peaks in the visible range (up to ~ 3 eV) are correspondingly observed at 1.89×10^5 , 3.58×10^5 , and $5.96 \times 10^5 \text{ cm}^{-1}$ respectively. Optical absorptions are further enhanced under applied pressure, the first observation being red shifting in absorption edge, and secondly shifting of absorption peaks towards the lower energy spectrum. Redshifting in absorption edge to 2.21, 1.82, and 1.07 eV (at 20 GPa for reference) is advantageous because lower photon energy can now be absorbed thus enhancing the PV's performance. Moreover, corresponding absorption peaks in the visible range are respectively enhanced for the same photon energy 4.12×10^5 , 6.48×10^5 , and $9.40 \times 10^5 \text{ cm}^{-1}$ (at 20 GPa for reference) indicating enhanced photon absorption under pressure. These results indicate that pressure has a

promising effect on the prospects of CSCs as absorbing material by simultaneously broadening the photon energy absorption range and magnitude in absorption coefficient.

Calculated OBG using Tauc [74] plot for CSCs under different pressures are displayed in Fig.S3 and Fig.S4. Corresponding OBG along with other optical parameters are presented in Table 4. At 0 GPa, the direct OBG (E_g^{opt}) for Cu_3NbS_4 and Cu_3NbSe_4 are predicted to be 2.74 and 2.41 eV respectively which is in good agreement with experimental band gaps. Consequently, our predicted OBG of 1.85 eV could be contemplated as accurate in the absence of experimental evidence for Cu_3NbTe_4 . The OBGs consequently decrease with pressure as already projected by ε_2 and η resulting in E_g^{opt} to vary from 2.74 to 1.28 eV for the compounds. This expresses that E_g^{opt} could be favourably tuned to the aforementioned desired range for potential optoelectronics applications.

3.4. Thermoelectric properties

The semiclassical Boltzmann transport theory proposes that electrons obey classical equations of motion between scattering events separated by a relaxation time while relying on the quantum-mechanical calculation of the electronic states. Within the CRTA as well as RTA according to BoltzTraP code, this work presents electron transport coefficients such as the Seebeck coefficient (S) which is the potential difference generated when two ends of a TE material are maintained at different temperatures, electrical conductivity (σ), total thermal conductivity (κ_T), which is determined by two parts: the electronic part (κ_e) and the lattice part (κ_l), TE power factor (PF), and TE figure of merit (ZT). The TE properties are computed using GGA+U+SOC formalism that best predicts the band gaps. The consideration of SOC for such calculation includes relativistic effects due to the presence of heavy atoms. Based on the semi-classical Boltzmann theory as implemented in BoltzTraP code, the TE parameters are calculated using the formulae [77]

$$S_{\alpha\beta}(\mu, T) = \frac{1}{eTV\sigma_{\alpha\beta}(T, \mu)} \int \bar{\sigma}_{\alpha\beta}(\mu - \epsilon) \left[\frac{\partial f_{\mu}(T, \epsilon)}{\partial \epsilon} \right] d\epsilon \quad (17)$$

$$\sigma_{\alpha\beta}(\mu, T) = \int \bar{\sigma}_{\alpha\beta} \left[- \frac{\partial f_{\mu}(T, \epsilon)}{\partial \epsilon} \right] d\epsilon \quad (18)$$

$$\kappa_{e(\alpha\beta)}(\mu, T) = \frac{1}{e^2TV} \int \bar{\sigma}_{\alpha\beta}(\epsilon) (\mu - \epsilon)^2 \left[- \frac{\partial f_{\mu}(T, \epsilon)}{\partial \epsilon} \right] d\epsilon \quad (19)$$

Where α, β, μ, V , and f are the usual TE parameters as implemented in the code.

Eqs. (17) and (18) can then be combined to calculate the PF, which has the relation

$$\text{PF} = S^2 \sigma \quad (20)$$

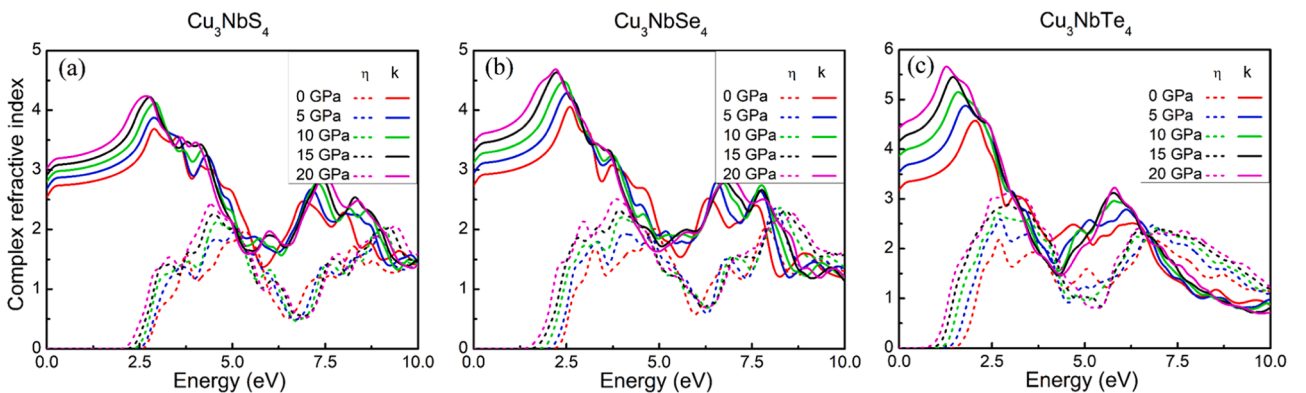


Fig. 5. Plot of η and k for Cu_3NbX_4 ($X=\text{S, Se, Te}$) obtained from DFT+U+SOC calculations.

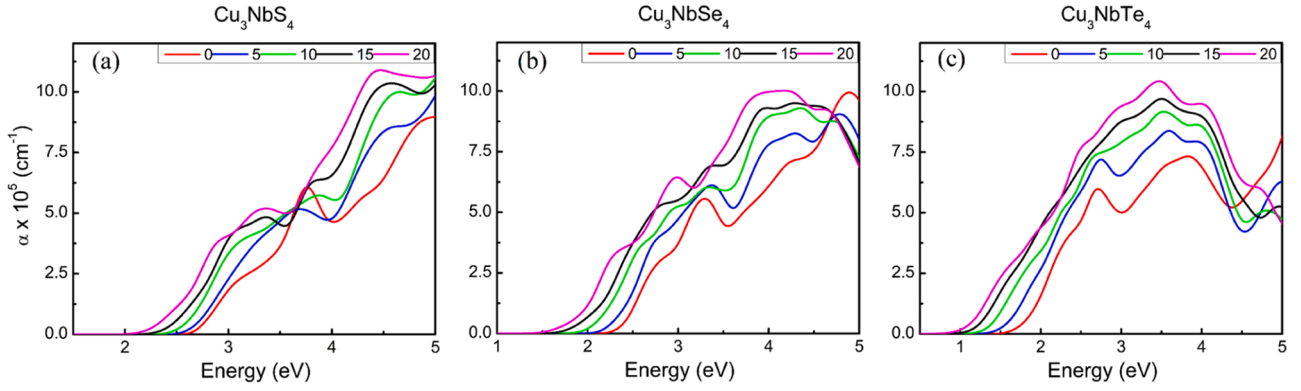


Fig. 6. Calculated α for Cu_3NbX_4 with colour codes in GPa pressure using DFT+U+SOC.

Table 4

Optical band gaps E_g^{opt} (eV), real part of static dielectric function ϵ_1 , refractive index η at 0 eV, and peak absorption α in the visible range (cm^{-1}).

Cu_3NbX_4	GPa	E_g^{opt} (This work)	E_g^{opt} (Other works)	$\epsilon_1(\omega)$	$\eta(0)$	$\alpha \times 10^5$
Cu_3NbS_4	0	2.74	2.50* [75], 2.60* [17], 2.56* [16], 3.47 [13], 3.21 [13], 2.31 [15]	6.58	2.56	1.89
	5	2.70	-	7.29	2.71	2.36
	10	2.59	-	7.96	2.82	3.40
	15	2.51	-	8.62	2.92	3.99
	20	2.39	-	9.21	3.03	4.12
Cu_3NbSe_4	0	2.41	2.45* [76], 2.20* [17], 2.13* [16], 2.64 [13], 2.75 [13], 1.95 [15]	7.54	2.75	3.58
	5	2.32	-	8.87	2.96	4.79
	10	2.15	-	9.84	3.12	5.25
	15	2.09	-	11.01	3.32	5.51
	20	1.93	-	11.95	3.47	6.48
Cu_3NbTe_4	0	1.85	1.46 [15], 2.24 [9], 1.08 [8]	10.34	3.18	5.96
	5	1.68	-	12.74	3.56	7.20
	10	1.52	-	15.12	3.86	7.90
	15	1.37	-	17.44	4.19	8.80
	20	1.28	-	19.64	4.43	9.40

* → Experiment.

A different approach is however implemented for calculating κ_l utilizing the Slack equation [78]

$$\kappa_l = A \frac{\bar{M} \delta \theta^3}{\gamma^2 n^{2/3} T} \quad (21)$$

Here $\bar{M}$, δ , n , γ , and T are average atomic mass, cube root of volume per atom, number of atoms per unit cell, Grüneisen parameter, and absolute temperature respectively while other parameters are already defined. The coefficient A can be further expressed as

$$A = \frac{0.5 \times 5.72 \times 10^7 \times 0.849 \gamma^2}{\gamma^2 - 0.514 \gamma + 0.228} \quad (22)$$

Making use of Eqs. (17)–(19); for easier comparison S , σ , and κ_e are initially predicted as illustrated in Fig.S6 (a-c) within the CRTA ($\tau = 10^{-14}$ s). Electronic properties calculation already reveals a decrease in band gaps for $X = \text{S} < \text{Se} < \text{Te}$ as well as with pressure. For this same reason, the CSC compounds thus exhibit intensifying σ and κ_e while reduced S value with diminishing band gaps as expected. The Seebeck coefficient S is observed to vary in magnitude in the order $X = \text{S} > \text{Se} > \text{Te}$ and is inversely proportional to temperature. The decrease in S from

2000–1000 μVK^{-1} down the chalcogenide group can be understood from the gradual decrease in their band gaps. Further, CSCs are observed to exhibit high σ in the order of $10^6 - 10^5 \text{ Sm}^{-1}$. The electronic part of thermal conductivity κ_e is observed to show moderate values which could be beneficial for TE materials and is directly proportional to temperature. The proportionality with temperature is comprehensible that charge carriers possess more kinetic energy leading to an upsurge in magnitude. Pressure has a significant impact on all the aforementioned transport properties, which vary depending on whether band gaps increase or decrease with pressure in general as previously discussed. Finally, the power factor PF to chemical potential is presented in Fig. 7 using Eq. (20) with negative μ depicting p-type doping while positive μ for n-type doping.

Thermal conductivity is a measure of how temperature difference can be maintained across certain materials demonstrating that low κ_l is beneficial for TE devices which could aid in the long-term operation of such devices. As depicted in Fig. 8, the lattice part of thermal conductivity κ_l is calculated following Eq. (21). κ_l is found to decrease down the chalcogenide groups for each respective temperature and pressure. The maximum $\kappa_l = 11.46 \text{ Wm}^{-1}\text{K}^{-1}$ being observed at 0 GPa and 300K for Cu_3NbS_4 ; and minimum κ_l as low as 1.09 Wm^{-1} for Cu_3NbSe_4 at 10 GPa and 900K. The total thermal conductivity $\kappa_T = \kappa_l + \kappa_e$ is then obtained separately for p-type and n-type doping where κ_e is derived using the appropriate τ (RTA) as discussed in detail in the preceding section.

The reliability of CRTA remains to be confirmed for many compounds, the RTA using the deformation potential theory approach with effective mass approximation is implemented for transport study [79–83]. According to this theory, the relaxation time of charge carriers at certain temperature can be obtained by the formula

$$\tau = \frac{2\sqrt{2}C\hbar^4}{3(K_B T m^*)^{3/2} E^2} \quad (23)$$

where C is elastic coefficient, $\hbar$ reduced Planck's constant, K_B Boltzmann constant, T temperature, m^* effective mass, and E is deformation potential (Fig.S7) which can be further expressed as

$$E = \frac{\Delta E_{\text{edge}}}{\Delta l/l} \quad (24)$$

Here, ΔE_{edge} is band edge variation (VBM or CBM) under strain in their lattice parameters (l). Thus, considering VB and CB relaxation time τ can be obtained separately for p-type and n-type doping. Compound dependent τ is then obtained from Eq. (23) as given in Table 5.

Effective mass plays a significant role in the prediction of materials for potential TEs. Fig. 9 illustrates the relation of effective mass with pressure. Relatively lower or higher effective mass indicates how easily or difficult charge carriers can drift due to the influence of energy. From the figure, though minute variations might occur at certain pressures, it is observed that pressure reduces the effective masses of electrons and

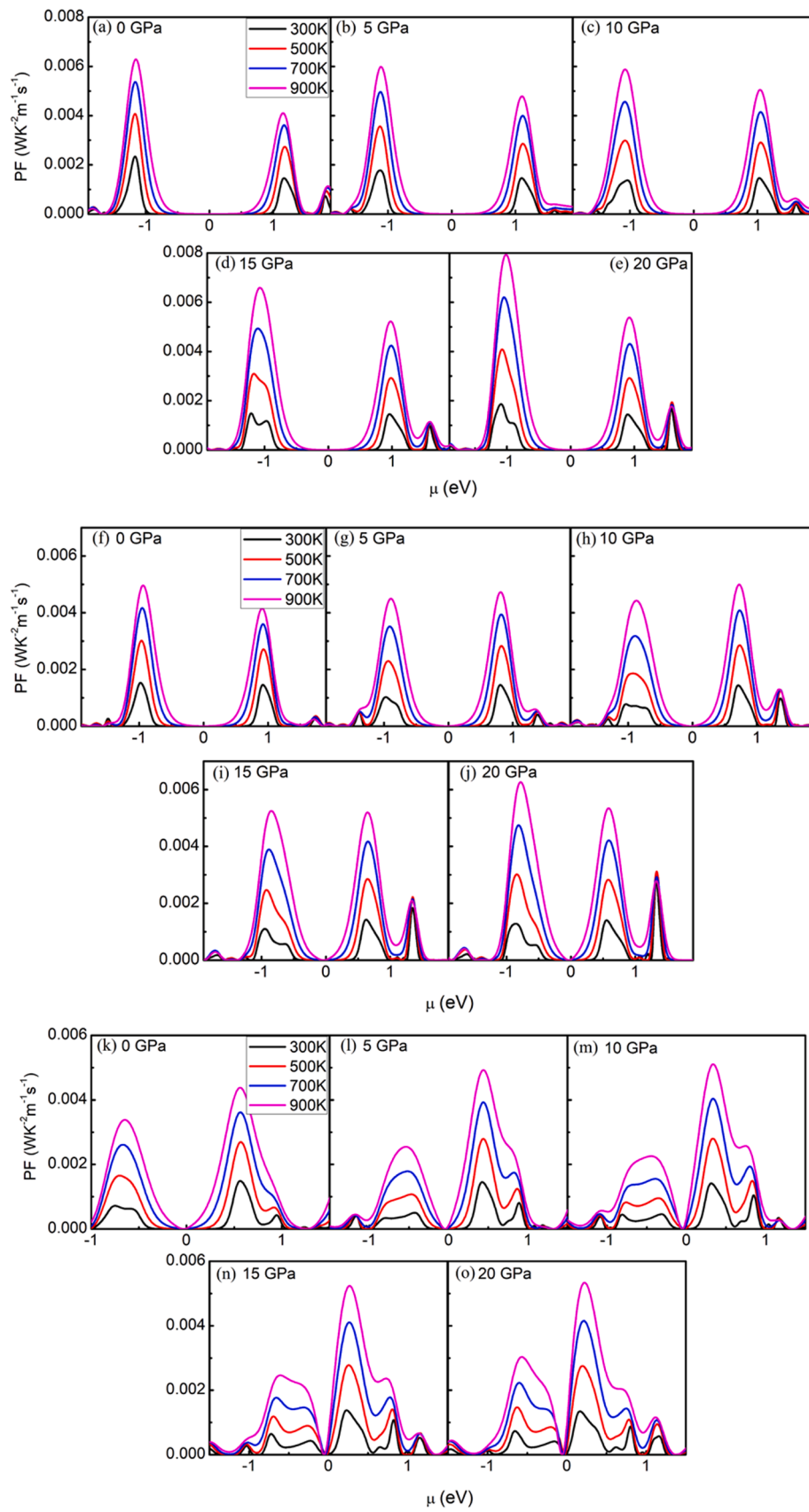


Fig. 7. Plot of PF at CRTA for (a-e). Cu_3NbS_4 , (f-j). Cu_3NbSe_4 , and (k-o). Cu_3NbTe_4 .

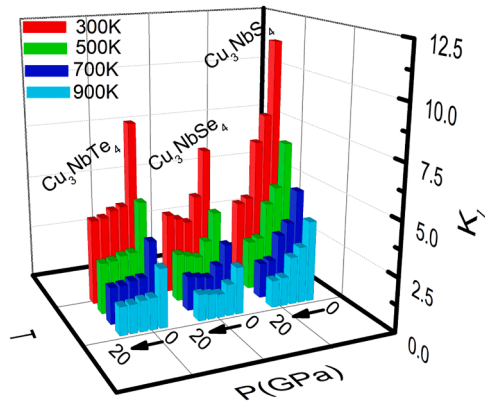


Fig. 8. Lattice part of thermal conductivity in units of $\text{Wm}^{-1}\text{k}^{-1}$.

Table 5

Calculated compound-dependent effective mass (m^*) and relaxation time (τ) from deformation potential.

Cu_3NbX_4	Doping type	Effective mass m^*	τ (300K)	τ (500K)	τ (700K)	τ (900K)
Cu_3NbS_4	p-type	1.143	$2.96 \times 10^{-14}\text{s}$	$1.37 \times 10^{-14}\text{s}$	$0.83 \times 10^{-14}\text{s}$	$0.57 \times 10^{-14}\text{s}$
	n-type	2.540	$1.49 \times 10^{-14}\text{s}$	$0.69 \times 10^{-14}\text{s}$	$0.42 \times 10^{-14}\text{s}$	$0.29 \times 10^{-14}\text{s}$
Cu_3NbSe_4	p-type	2.106	$0.63 \times 10^{-14}\text{s}$	$0.29 \times 10^{-14}\text{s}$	$0.18 \times 10^{-14}\text{s}$	$0.12 \times 10^{-14}\text{s}$
	n-type	1.992	$0.51 \times 10^{-14}\text{s}$	$0.24 \times 10^{-14}\text{s}$	$0.14 \times 10^{-14}\text{s}$	$0.10 \times 10^{-14}\text{s}$
Cu_3NbTe_4	p-type	0.724	$5.32 \times 10^{-14}\text{s}$	$2.47 \times 10^{-14}\text{s}$	$1.49 \times 10^{-14}\text{s}$	$1.02 \times 10^{-14}\text{s}$
	n-type	1.037	$2.14 \times 10^{-14}\text{s}$	$0.99 \times 10^{-14}\text{s}$	$0.60 \times 10^{-14}\text{s}$	$0.41 \times 10^{-14}\text{s}$

holes in general. This suggests transport properties enhancement concerning charge carriers. Moreover, this trend of gradual decrease in effective masses can be correlated to energy bands of Cu_3NbX_4 (see Fig. 3 and Fig.S2) where energy bands become more curved, especially in the VBM and CBM.

The TE figure of merit ZT is perhaps the most important factor that governs the performance of TE materials. It can be illustrated that though S and σ could independently contribute towards enhancement in ZT, it should be understood that these are contradicting properties as already mentioned in the introduction section. For this reason, obtaining a reasonable ZT for practical application is quite a challenging task.

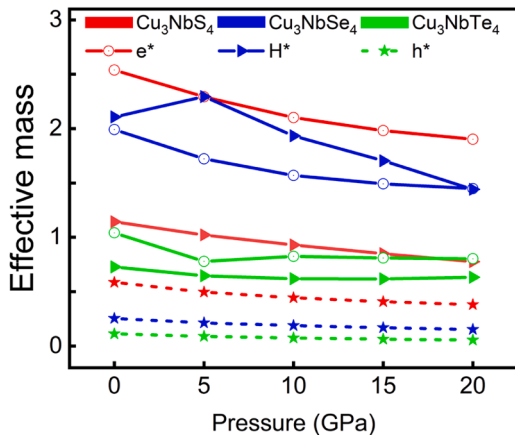


Fig. 9. Effective mass variation with pressure for Cu_3NbX_4 with colour coding specific for each compound while e^* , H^* , and h^* is effective mass of electron, heavy hole, and light hole respectively.

Calculated ZT against temperature up to 900K is presented in Fig. 10 by employing the formula $ZT = \frac{S^2 \sigma}{\kappa_T} T$ and τ as obtained from deformation potential theory. As calculated transport properties differ by only in factors of relaxation time ' τ ', separate plots for each property are thus not provided but rather directly implemented into the calculation of ZT. At ambient pressure, the minimum (300K) and maximum (900K) ZT are 0.14, 0.04, 0.10 and 0.40, 0.18, 0.42 respectively for $X = \text{S, Se, and Te}$ in the p-type doping. The abnormally low ZT for Cu_3NbS_4 however cannot be explained due to the diverse independent parameters. It is also noted that our results are much lower than other theoretically predicted ZT. Even at as low as 300K, Hong et al., [8] predicted ZT of 0.54 and 0.48 respectively for Cu_3NbSe_4 and Cu_3NbTe_4 . Further, Enamul Haque [7] independently reported ZT values of 0.275, 0.485, and 0.750 at the same temperature for Cu_3NbS_4 , Cu_3NbSe_4 , and Cu_3NbTe_4 respectively. Moreover, at 1000K both article reports $ZT > 1$ for these investigated compounds. However, when compared with experimental results from Chen, E.M. et al., [17] where authors report astonishingly low ZT in the order 10^{-5} ; our calculations seem to align closer to available experimental results. The CSCs possessing wide band gaps intrinsically show low TE properties subsequently resulting in low ZT. With such low ZT of CSCs under ambient pressure, this study further investigates TE efficiency for enhanced ZT under pressure from all the positive hints acquired in the previous discussions like narrowing of band gaps, lower effective mass, lower κ_l , enhanced transport properties, etc. ZT values are slightly enhanced under pressure for all the CSCs both in the p-type and n-type doping with maximum values of 0.58, 0.26, and 0.48 for $X = \text{S, Se, and Te}$ respectively. Surprisingly, for Cu_3NbTe_4 is visibly reduced at 20 GPa which is attributed to the drastic reduction in Seebeck coefficient exhibiting the minimum S value among all the CSCs under pressure. Minor secondary peaks observed at around +1.3 eV of μ at certain pressures arrive from the deeper/higher energy bands which play no significant role in predicting the TE efficiency. This is due to supplementary energy demands from such states to make meaningful contributions towards TE performance. If however, such peaks are relatively higher than those near the Fermi level, they might still be advantageous for TE provided the energy variation is minimal.

4. Conclusion

Nb-based copper sylvanite compounds have been successfully investigated within DFT based computational approach and BoltzTraP simulations. The calculated optical band gaps of 2.74 and 2.41 eV respectively for Cu_3NbS_4 and Cu_3NbSe_4 provide accurate results closer to experimental values. Following a similar approach, our predicted optical band gap of 1.85 eV for Cu_3NbTe_4 can be considered accurate and thus could contribute valuable data for future scientific research. As for the prospects of Cu_3NbX_4 ($X = \text{S, Se, Te}$) for optoelectronics, the compounds already possess good absorption in the order of 10^{-5} cm^{-1} even at 0 GPa pressure. Moreover, the band gap decreases with pressure resulting in the onset of optical activity to redshift as well as results in enhanced absorption in the IR-vis region which is ideal for PV's. The investigated compounds also reveal moderate ZT which is quite lower than already existing theoretical reports and is however closer to available experimental results. The present research work not only provides new insights into Cu_3NbX_4 for potential light energy harvesting but also towards their experimental synthesis due to outstanding mechanical and dynamical stabilities as indicated from respective *ab initio* stability results.

CRedit authorship contribution statement

Bernard Lalroliana: Writing – original draft, Visualization, Investigation, Formal analysis, Data curation. **Lalmuan chhana:** Methodology, Conceptualization. **Lalhum hima:** Visualization, Data curation. **R. Zosiamliana:** Formal analysis, Data curation. **Shivraj Gurung:**

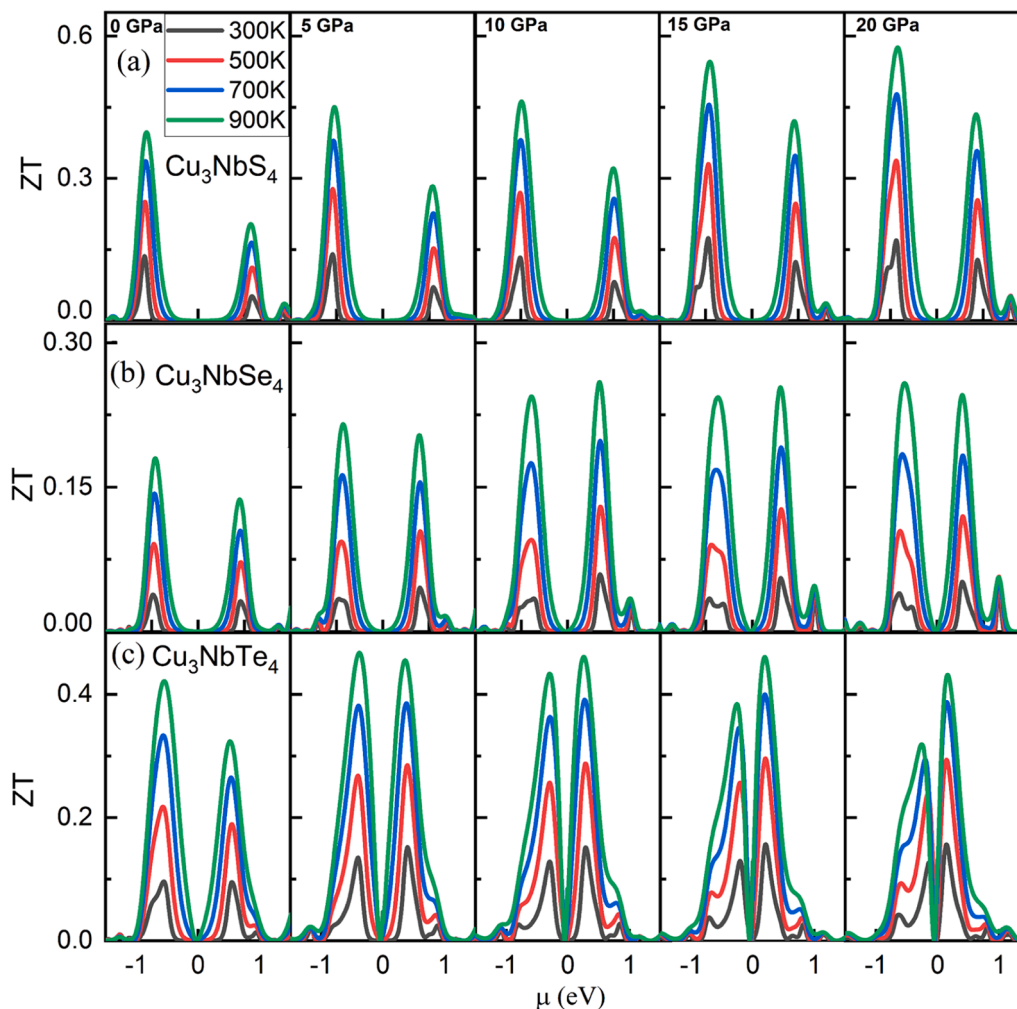


Fig. 10. Calculated ZT using appropriate RTA for (a) Cu_3NbS_4 (b) Cu_3NbSe_4 (c) Cu_3NbTe_4 .

Software, Resources, Data curation. **Lalhriat zuala:** Writing – review & editing, Supervision, Software, Resources, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.materresbull.2024.113054](https://doi.org/10.1016/j.materresbull.2024.113054).

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PAPER



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Enhanced optical and thermoelectric properties of $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ through chemical substitution: a DFT approach

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This study presents theoretical investigations of a $2 \times 2 \times 2$ supercell structure of $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ ($x = 0.00, 0.25, 0.50, 0.75, 1.00$) for optoelectronic and thermoelectric applications within DFT. Formation energy calculation reveals the energetical favourability of predicted compounds under chemical substitution. Electronic properties are investigated to comprehend the effect of V substitution on the Nb site. Results are then correlated with optical and thermoelectric properties. The study reveals a reduction in energy band gap with enhanced optical absorption coefficient in the order of 10^5 cm^{-1} and maximum $ZT = 0.83$ at 1100 K for certain substitution levels, revealing prospects of the investigated supercell for potential optoelectronic and thermoelectric devices. Systematic investigation into supercells' properties is expected to provide a relevant approach towards future investigations on doping or chemical substitutional research.

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1 Introduction

Substitutional doping significantly influences semiconductor devices, altering their mechanical, electronic, optical, and transport properties through induced changes. This technique is particularly valuable in semiconductor physics, enhancing stability and carrier mobility in certain cases. The concentration of dopants/substituting atoms is crucial for modifying these properties, demonstrating a clear concentration-dependent relationship. The choice of a suitable replacement atom is essential for advancing technology and device applications. For instance, zinc doping enhances the catalytic activity of graphene for CO oxidation, which is otherwise inert in its pristine form.¹ Additionally, K and I co-doping in $\text{g-C}_3\text{N}_4$ results in a dramatic increase in its photoelectrochemical performance, as reported by Jing *et al.*² A 40% increase in the dimensionless thermoelectric figure of merit (ZT) was observed with doping in AgSbTe_2 , raising its ZT value to 1.35.³ Independent studies on aluminium nitride (AlN) co-doped with Mg–Hf and Mg–Zr unveiled remarkable enhancements in piezoelectric properties.⁴ Numerous articles highlight the beneficial effects of chemical substitution across various fields,

including optoelectronics, thermoelectricity, catalysis, mechanical enhancement, sensors, photocatalytic properties, magnetism, *etc.*^{5–11} Thus, it can be inferred that substitutional doping enables precise control over electronic properties, which play a significant role in designing and fabricating efficient devices.

The quest for Earth-abundant materials with adjustable band gaps in the 1–3 eV range is motivated by their potential for optoelectronic and thermoelectric applications.¹² In particular, certain copper chalcogenides featuring a cubic sulvanite structure, such as Cu_3TMQ_4 (where $\text{TM} = \text{V}, \text{Nb}, \text{Ta}$ and $\text{Q} = \text{S}, \text{Se}, \text{Te}$), have gained interest due to their compositional versatility. This adaptability enables significant band gap engineering, ranging from 1.3 eV for Cu_3VS_4 to 2.83 eV for Cu_3TaSe_4 , achieved through selective substitution of elements.^{13,14} These materials hold promise for applications in solar water splitting,¹⁵ photovoltaic devices,¹⁶ transparent conducting materials for laser diodes, light emitting diodes,¹⁷ flat panel displays,¹⁸ thermoelectric devices,¹⁹ *etc.* Thin film investigations into the sulvanite compounds have been performed for Cu_3TaS_4 and Cu_3TaSe_4 by Newhouse *et al.*,²⁰ which were fabricated on an amorphous SiO_2 substrate through *ex situ* annealing and a pulsed laser deposition method (PLD). García *et al.*²¹ and Guillén *et al.*²² proposed similar approaches for achieving potential transparent conducting materials through doping. Lv *et al.*²³ prepared a 220 nm thick Cu_3VS_4 thin film on a glass substrate using a similar synthesis method, revealing high absorption coefficients of the order of 10^5 cm^{-1} suggesting potential applications in solar photovoltaics (PV).

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They also reported a transition from an indirect band gap to a near-direct band gap of 1.35 eV with high electrical conductivity as the structure changed from bulk to thin films. In recent years, Syu and co-workers²⁴ developed a prototype Cu_3VS_4 thin film for light absorbers where a maximum power conversion efficiency of 3.11% is achieved. Mantella and co-workers²⁵ express the size dependent optical properties of sylvanite nanocrystals. Notably, the only doping investigations on copper sylvanite compounds were conducted by Chen *et al.*,²⁶ who synthesized various compositions of $\text{Cu}_3\text{NbS}_{4-x}\text{Se}_x$, and S. Ikeda *et al.*,²⁷ who explored chemical substitution in $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ for photocatalytic and photoelectrochemical H_2 evolution. Chen's study found that the doped structure still resembles the parent Cu_3VS_4 cubic crystal, with an increased lattice parameter, successfully tuning the optical band gaps (E^{opt}) from 2.6 to 2.2 eV while enhancing the optical absorption and thermoelectric performance. Though Cu_3TMQ_4 exhibits potential applications in the field of optoelectronic and thermoelectric devices, investigations require not only a robust and high-throughput theoretical framework but also experimental validation as put forward by I. Caro-Campos *et al.*²⁸ in 2024, which otherwise could lead to diverse results for the same calculation. This is especially significant for theoretical predictions since band gaps play a crucial role in optoelectronic and thermoelectric devices as major contributions to these properties arrive directly from electronic properties. This suggests that, particularly for Cu-based copper sylvanites, comparing DFT results with experimental data is critical for validating theoretical conclusions; consequently, this study will try its best to compare our results with available experimental data.

Upon reviewing various literature sources, the importance of chemical substitution with appropriate atoms becomes evident. However, there is a clear lack of studies on chemical substitution and doping in Cu_3TMQ_4 compounds. Therefore, we have undertaken an investigation into chemical substitution in a $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell (SC) using first principles to examine its effects on the mechanical, electronic, optical, and thermoelectric properties.

2 Computational details

The projector augmented wave (PAW)²⁹ potential based *ab initio* studies into $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ have been performed using MedeA-VASP 5.4^{30–32} within the GGA-PBE³³ formalism. The pseudopotential for each element S, V, Cu, and Nb is specified which treats $3s^23p^4$, $3s^23p^63d^44s^1$, $3d^{10}4s^1$, and $4s^24p^64d^55s^1$ respectively as valence electrons. The already well explored bulk cubic crystal, Cu_3NbS_4 , functions as the parent compound for the substitutional doping. After full structural optimization of the bulk crystal using an $8 \times 8 \times 8$ k -mesh, 0.02 eV $\text{\AA}^{-1}$ ionic relaxation, and 400 eV kinetic energy cut-off, a $2 \times 2 \times 2$ supercell is modelled consisting of 64 atoms. Geometrical optimization was then performed in the SC with $4 \times 4 \times 4$ k -point sampling in the Monkhorst pack scheme.³⁴ The code's default settings for bulk compounds employed $4 \times 4 \times 4$ k -mesh, 0.02 eV $\text{\AA}^{-1}$ ionic relaxation, and a kinetic energy cut-off of around 300 eV.

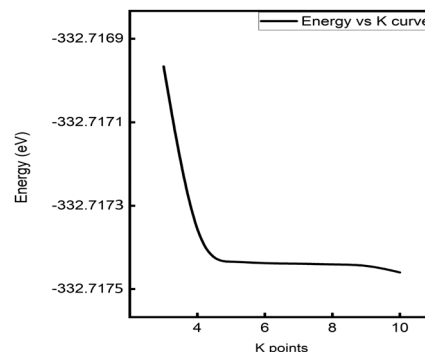


Fig. 1 Total energy convergence test with respect to K points.

To ensure accurate calculations, a much tighter convergence is employed as discussed above. Fig. 1 demonstrates the convergence test for the adopted k -points, where energy remains consistent up to three decimals. The decrease in k -mesh by a factor of 2 is due to an increase in real space dimensions of the supercells, subsequently decreasing in equal proportions in their reciprocal space thus demanding lesser k -points for the same accuracy. A dense $6 \times 6 \times 6$ k -mesh with a kinetic cut-off energy of 400 eV and an SCF convergence of 10^{-5} eV was employed for electronic property calculations. Due to the semiconducting nature of the investigated compounds, the tetrahedron method with Blöchl correction was used for integration in the first Brillouin zone.³⁵ A denser k -mesh of $13 \times 13 \times 13$ was used for electron transport calculations using BoltzTraP code. The Nb atoms are then substituted with V atoms from the pristine SC so that it takes the chemical formula $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ ($X = 0.00, 0.25, 0.50, 0.75, 1.00$) wherein similar calculations for properties were then re-performed for investigation under chemical substitution.

For stability examinations, this study employs formation energy calculation, which has been widely adopted for stability predictions.^{36–40} The calculation follows the formula:^{41,42}

$$E_{\text{form}} = \frac{1}{N} \left(E_{\text{total}}^i - \sum n_z E_z^{\text{bulk}} \right) \quad (1)$$

E_{form} is the resultant formation energy, N is the total number of atoms in the supercell, E_{total}^i is the total energy of SC, and n_z is the total number of elements corresponding to energy E_z^{bulk} . Negative E_{form} indicates the amount of energy released for the SC formation, indicating additional relative stability for larger values, while positive E_{form} indicates additional relative instability as energy will be required for the formation of such supercells. Calculated E_{form} values using eqn (1) are provided in Table 1 all showing negative values, revealing the ground state energetical stabilities of the SCs.

It is acknowledged that the bulk crystals of Cu_3NbS_4 , $\text{Cu}_3\text{Nb}_{0.50}\text{V}_{0.50}\text{S}_4$ and Cu_3VS_4 ($X = 0, 0.5$ and 1.0) had already been synthesized experimentally.²⁷ Furthermore, E_{form} remains consistent with these already synthesized compounds throughout the substitution process, implying that the SCs may likewise be stable for experimental synthesis at $X = 0.25$ and 0.75 substitutions.

Table 1 Computed formation energy for $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ in units of eV

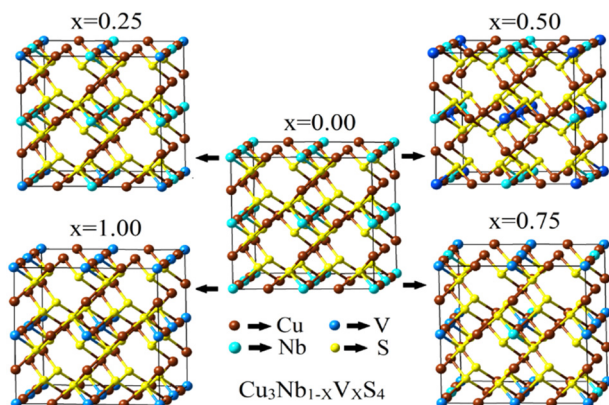
$\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$	E_{total}^i	$n_{\text{Cu}}E_{\text{Cu}}^{\text{bulk}}$	$n_{\text{V}}E_{\text{V}}^{\text{bulk}}$	$n_{\text{Nb}}E_{\text{Nb}}^{\text{bulk}}$	$n_{\text{S}}E_{\text{S}}^{\text{bulk}}$	E_{form}
$X = 0.00$	−342.90	−89.52	00.00	−40.88	−108.48	−0.99
$X = 0.25$	−340.34	−89.52	−08.99	−30.66	−108.48	−0.98
$X = 0.50$	−337.80	−89.52	−17.98	−20.44	−108.48	−0.98
$X = 0.75$	−335.26	−89.52	−26.97	−10.22	−108.48	−0.98
$X = 1.00$	−332.74	−89.52	−35.96	00.00	−108.48	−0.98

3 Results and discussion

3.1. Structural and mechanical properties

The crystal structure of Cu_3NbS_4 is optimized to the $P\bar{4}3m$ symmetry space group with 5.53 Å lattice constant, which is consistent with the reported work.^{26,43} Resultant SCs for various V-substitution after optimization are shown in Fig. 2. The calculated lattice parameter as given in Table 2 shows that Nb replacement does affect its structural property with a slight decrease in lattice parameter from 11.06 to 10.84 Å. The equivalent lattice constants for the same are 5.53 and 5.42 Å respectively, which agree well with experimental values of 5.50 and 5.39 Å.⁴⁴ Our theoretical results differ from experimental values by just 0.55% and 0.56% and hence are regarded as accurate for property investigation. Also, Nb replacement with V seems to preserve the cubic nature of the compounds, which agrees with the reported work on doping of S by Se.²⁶

The mechanical properties of the $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell are generated according to ref. 45 and 46. Elastic moduli such as bulk modulus (B), shear modulus (G), Young's modulus (Y), Poisson's ratio (ν), and Pugh's ratio (B/G) are calculated within

**Fig. 2** Optimised $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell structures, where $X = 0.00, 0.25, 0.50, 0.75$, and 1.00 .

the formalism of Hill assumptions^{47,48} along with their Debye temperature (θ)⁴⁹ and Grüneisen parameter (γ).^{50,51}

For cubic crystals, three elastic constants C_{11} , C_{12} , and C_{44} are required for the prediction of various elastic properties. Elastic properties like B , G , Y , ν , and γ within Hill's assumption can be derived by prior consideration of Voigt⁵² (subscript V) and Reuss⁵³ (subscript R) assumption.

$$B_V = B_R = \frac{(C_{11} + 2C_{12})}{3} \quad (2)$$

$$G_V = \frac{(C_{11} - C_{12} + 3C_{44})}{5}, \quad G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3C_{11} - 3C_{12}} \quad (3)$$

From eqn (2) and (3), elastic properties within Hill's assumption can be derived following the formula

$$B = \frac{B_V + B_R}{2}, \quad G = \frac{G_V + G_R}{2} \quad (4)$$

Subsequently, Y and ν can be calculated

$$Y = \frac{9BG}{3B + G}, \quad \nu = \frac{3B - 2G}{2(3B + G)} \quad (5)$$

$$\gamma = \frac{3}{2} \left(\frac{1 + \nu}{2 - 3\nu} \right) \quad (6)$$

Finally, the mean sound velocity can be obtained as

$$u_m = \left[\frac{1}{3} \left(\frac{2}{u_t^3} + \frac{1}{u_l^3} \right) \right]^{-\frac{1}{3}} \quad (7)$$

where u_t and u_l are transverse and longitudinal sound velocities respectively and ρ is the density

$$u_t = \left(\frac{G}{\rho} \right)^{\frac{1}{2}} \text{ and } u_l = \left(\frac{3B + 4G}{3\rho} \right)^{\frac{1}{2}} \quad (8)$$

The various mechanical properties obtained using the appropriate formulas and equations are shown in Table 2. B predicts resistance towards axial deformation while shear strain resistance can be inferred from G . The SCs are found to possess greater axial resistance than shear resistance as indicated by the relatively higher magnitude of B over G . Moreover, the bulk modulus (B) also signifies resistance towards volume change. Chemical substitution at $X = 0.25$ results in an abrupt increase in B , which eventually decreases as the concentration is raised till $X = 0.75$. But when Nb-atoms are fully replaced by V-atoms, the bulk modulus (B) slightly rises again indicating Cu_3NbS_4 to be relatively softer than Cu_3VS_4 towards volume change. The

Table 2 Supercell lattice constant a (Å), bulk modulus B (GPa), shear modulus G (GPa), Young's modulus Y (GPa), Poisson's ratio ν , Pugh's ratio B/G , Debye temperature θ (K), and Grüneisen parameter γ

$\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$	a	C_{11}	C_{12}	C_{44}	B	G	Y	ν	B/G	θ	γ
$X = 0.00$	11.06	95.40	12.40	28.32	40.07	33.02	77.71	0.18	1.21	339.1	1.20
$X = 0.25$	11.01	102.72	20.90	29.21	48.17	33.44	81.46	0.22	1.44	346.2	1.36
$X = 0.50$	10.96	97.92	17.44	28.06	44.27	32.43	78.19	0.21	1.36	344.2	1.31
$X = 0.75$	10.90	95.39	15.70	25.53	42.26	30.53	73.83	0.21	1.38	326.4	1.32
$X = 1.00$	10.84	96.25	19.25	25.01	44.92	29.75	73.10	0.23	1.51	335.3	1.40

ductility of a material can be obtained from Poisson's (ν) and Pugh's ratio (B/G). The critical limits for these two quantities are $\nu = 0.28$ and $B/G = 1.75$. Below these limits, the materials/compounds are considered brittle. All the calculated values are below these critical limits demonstrating the brittle nature of the SCs. This brittle nature of the SCs could be an advantage in device fabrication as brittle materials and almost ductile materials can easily cleave off to form discontinuous chips rather than clumping up when chipped.

3.2. Electronic properties

To gain a better understanding of the compounds, it is vital to analyze the electronic band structure of the predicted compounds. Several investigations have implemented first-principles calculations to investigate the electronic structure of copper sylvanite compounds. These reports reveal that the compounds are indirect band gap semiconductors exhibiting a wide range of band gaps.^{54–56} Calculated electronic band structures with their corresponding PDOS are shown in Fig. 3. The notable observation is the seeming transition to direct band gap nature from indirect band gap nature at the Γ -high symmetry point. This arises because as lattice dimensions in real space expand, it results in an increase in the number of atoms due to the $2 \times 2 \times 2$ SC. On this account, the first Brillouin zone (BZ) in reciprocal space diminishes to exactly half and more lines populate the band structure and band folding arises.^{57,58} This indicates that this seeming transition is perhaps due to band folding. Predicted band gaps for $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercells are 1.68, 1.29, 1.13, 1.08, and 1.03 eV for $X = 0.00$, 0.25, 0.50, 0.75, and 1.00 respectively. At $X = 0.00$ and 1.00, band gaps are respectively comparable to other theoretical data of Cu_3NbS_4 and Cu_3VS_4 .^{21,22,59} From Fig. 3(a), major contribution in the conduction band (CB) arrives from Nb-d atomic orbitals with a possible minor contribution from hybridized states of S-p and Cu-d orbitals. Furthermore, in the valence band (VB) minor

equivalent contribution near the Fermi level ($E_F = 0$ eV) is observed from all possible hybridized states of S-p, V-d, and Cu-d orbitals while Cu-d has a major influence on the deeper energies (-1.2 eV) leading to the unique electronic band profile.

The PDOS contributions from different atomic valence orbitals are further divided as illustrated in the figure description according to bonding pairs and atomic positions in the SC. In the presence of Nb and V atoms, it is perceptible that contributions near the E_F by Nb atoms are suppressed, which is evident from higher V concentrations (Fig. 3(c) and (d)). Chemical substitution at $X = 0.25$ results in the formation of isolated and unique energy bands that constitute the CB edge. Formation of the depleted energy band like gap is observed around 1.3 eV which is revealed by the devoid of PDOS. These bands lead to the sudden decrease in band gap by an astonishing 0.39 eV resulting in the highest band gap shift due to substitution. The corresponding set of PDOS peaks is mainly revealed by blue, green, and black colour curves each representing V-d, Cu-d(V, Nb), and S-p(V) orbital contribution respectively. It is evident that the V-atom has a great influence on the existence of this PDOS peak while Nb primarily contributes only to higher energy bands in the CB; thus, there is a decrease in band gaps with V substitution on Nb sites. Surprisingly, the same atomic orbitals exhibit different magnitudes of PDOS according to their bonding and atomic positions. In a general sense, relatively higher PDOS could signify a higher contribution by that particular atom (orbitals) in the formation of that respective compound and *vice versa*. Accordingly, V has higher PDOS than Nb signifying greater orbital contribution towards the compound formation. This could be due to the higher electronegativity of V than Nb from Paulin's electronegativity scale implying relatively higher reactivity for V. Perhaps for this same reason, the PDOS contributions from Cu-d(V, Nb) and S-p(V) are thus higher than those of Cu-d(Nb, Nb) and S-p(Nb) respectively. Following this trend, especially in the CB, we can anticipate that atoms in and around having a maximum number of V atoms will have maximum PDOS contribution in the energy band profile. The electronic band structures with PDOS at $X = 0.50$ V are shown in Fig. 3(c). In this level of chemical substitution, equal numbers of V and Nb atoms (4 each) are present in the SC with a visible diminishing band gap due to the shifting of the band edge towards the E_F from the CB. Also, distinct discontinuities of bands continue to occur around the same energy where depletion in PDOS was previously observed. Though diverse atomic orbitals contribute to these peculiar isolated bands in the CB, negligible contribution arrives from Nb atomic orbital states. Distinct PDOS values for Cu-d(V, V), Cu-d(V, Nb), and Cu-d(Nb, Nb) are also observed with varying magnitudes as expected. When V is increased to 0.75, the decrease in band gaps continues and previously observed isolated energy bands become almost continuous with the higher energy bands. As expected, V contribution now becomes overwhelmingly large both in the VB and the CB as compared to Nb. All these findings led to the understanding of the sudden drop followed by the gradual decrease of the energy band gap in the investigated SC from 1.29 eV at $X = 0.25$ to 1.03 eV at $X = 1.00$.

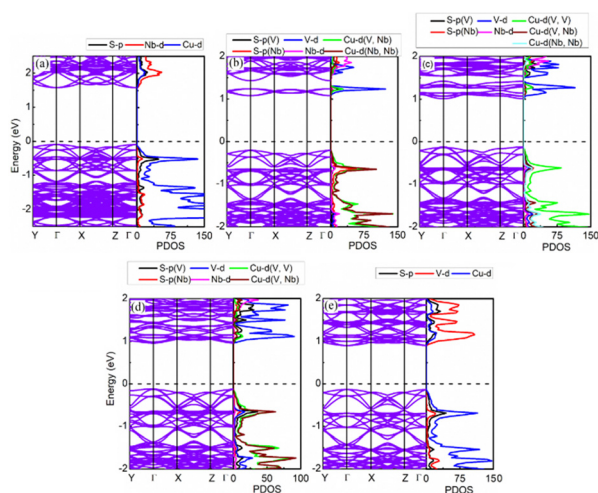


Fig. 3 Band structure with the corresponding PDOS (states per eV) of $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$. (a) $X = 0.00$, (b) $X = 0.25$, (c) $X = 0.50$, (d) $X = 0.75$, and (e) $X = 1.00$. Here S-p(Z) corresponds to S atoms bonded to Z atoms, and Cu-d(A, B) corresponds to Cu atoms sandwiched between A and B atoms in the SCs.

3.3. Optical properties

The interaction of materials when exposed to incident radiation can be understood from the analysis of optical properties and this study investigates the optical properties by computing the complex dielectric constants, complex refractive index, absorption coefficient, and theoretical optical band gap $E^{\text{opt}}(\text{DFT})$ as a function of photon energy for the $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell as illustrated in Fig. 4. The first to be investigated is perhaps the dielectric function which consists of the real part ε_1 and the imaginary part ε_2 . It is also from this function that all other optical properties can be subsequently derived from. The complex function can be expressed in the following equation:⁶⁰

$$\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2 \quad (10)$$

From this, supplementary optical properties like refractive index (η) and extinction coefficient (k) can be directly obtained as follows:⁶¹

$$\eta(\omega) = \frac{1}{\sqrt{2}} \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{1/2} \quad (11)$$

$$k(\omega) = \frac{1}{\sqrt{2}} \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega) \right]^{1/2} \quad (12)$$

For further investigation into the SC for potential photovoltaic absorbers, it is essential to examine the absorption coefficient (α) from the extinction coefficient using the formula

$$\alpha(\omega) = \frac{4\pi k(\omega)}{\lambda} \quad (13)$$

The complex dielectric function plot for various levels of substitution is illustrated in Fig. 4(a). The real part of dielectric function ε_1 typically measures the polarization of certain materials due to incident radiation. The dielectric constant is determined when no photon falls on the material, *i.e.* $\varepsilon_1(0)$, and is calculated to be 7.86, 8.22, 8.46, 8.70, and 9.05 arb. unit respectively for $X = 0.00, 0.25, 0.50, 0.75$, and 1.00 . ε_1 is closely related to the refractive index η as shown in Fig. 4(b). The η also provides us with additional information on anomalous

dispersion which is of importance, especially in the visible energy range for potential PV applications. Anomalous dispersion will occur in regions where η decreases with an increase in photon energy. This is a significant notable consequence as this often arises in regions of strong optical absorption. Initially, η peaks drastically red shift at $X = 0.25$ gradually decreasing with an increase in X . This ultimately could indicate strong optical absorption in the lower photon energies. The characteristic trend is followed by $\varepsilon_1(\omega)$ and hence by η for certain Nb replacements except at $X = 0.00$, where there exists a unique sudden change in the plot due to the absence of V atoms.

The interband transitions can be mostly defined from the imaginary part of the dielectric function ε_2 which is closely related to the extinction coefficient k that further correlates to the absorption coefficient α employing eqn (13). The ε_2 and perhaps k maintain the zero magnitudes for certain specific photon energy after which continuous optical activity persists for a higher photon energy range. At $X = 0.00$ and 0.25 , the electronic band profile and thus resultant optical properties vary significantly. Minute optical activity exists for $\text{Cu}_3\text{Nb}_{0.75}\text{V}_{0.25}\text{S}_4$ at ~ 1.82 eV due to interband transition between the unique PDOS peaks in the CB and S-p, Cu-d states in the VB. This optical activity for a particular photon energy of ~ 1.82 eV vanishes for $X = 0.00$ as it falls well below the $E^{\text{opt}}(\text{DFT})$ (see Fig. 5). Moreover, stronger optical activity exists in higher photon energy for the

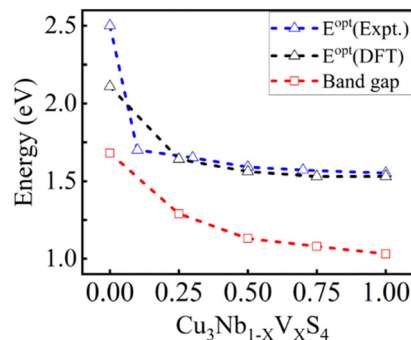


Fig. 5 Variation of experimental $E^{\text{opt}}(\text{Expt.})$, $E^{\text{opt}}(\text{DFT})$, and fundamental energy band gaps (eV) in $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$.

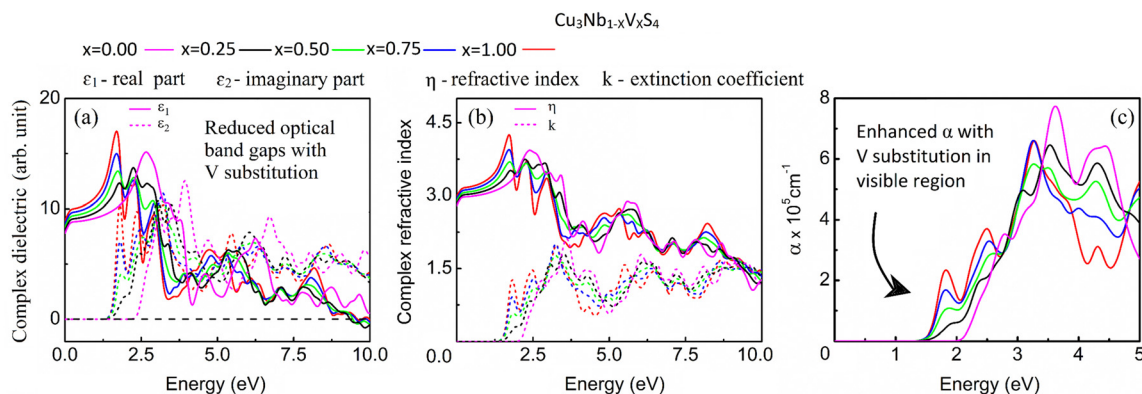


Fig. 4 Calculated optical properties of $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$: (a) dielectric function, (b) refractive index and extinction coefficient and (c) absorption coefficient.

Cu_3NbS_4 and the $\text{Cu}_3\text{V}_{0.25}\text{Nb}_{0.75}\text{S}_4$ supercell due to the participation of deeper/higher energy bands from both the CB and VB. At higher concentrations of $X = 0.50, 0.75$, and 1.00 , first optical peaks are observed at ~ 1.82 eV which corresponds to the interband transition between the Cu-d and V-d states in general. Furthermore, the second optical peaks are observed at ~ 2.42 eV after a dip in magnitude which corresponds to the transition between the same states but from higher energies in the CB. This can be understood due to the presence of multiple PDOS peaks which provide additional states for direct transitions. The $\text{Cu}_3\text{Nb}_{1-X}\text{V}_X\text{S}_4$ supercell exhibits a good absorption coefficient α in the order of 10^5 cm^{-1} at all levels of V-substitution as shown in Fig. 4(c). With regards to prospects for optoelectronics, our investigated SC with a thickness of 100 nm could strongly absorb photons, paving the path for potential PV for certain V-substitution in the visible region. The onset of α is utilized for predicting $E^{\text{opt}}(\text{DFT}) = 2.11, 1.64, 1.56, 1.53$, and 1.53 eV respectively for $X = 0.00, 0.25, 0.50, 0.75$, and 1.00 . Our predicted values are comparable to experimental optical band gaps $E^{\text{op}}(\text{Expt.})$ reported by Ikeda *et al.*,²⁷ where band gaps are obtained from their absorption edge, analogous to our theoretical approach for predicting $E^{\text{opt}}(\text{DFT})$. The $E^{\text{opt}}(\text{DFT})$ consistency at $X = 0.75$ and 1.00 can be realized from their comparable electronic band structures. A pictorial representation of band gap variation with certain V concentrations is illustrated in Fig. 5 for easier comparison.

3.4. Thermoelectric properties

Transport properties for predicting TE properties are carried out following the semi-classical Boltzmann transport theory. This theory suggests that electrons follow classical equations of motion between scattering events separated by relaxation time, while depending on the quantum-mechanical calculation of the electronic states. Within the default constant relaxation time approximation (CRTA) of $\tau = 10^{-14}$ s as implemented in the BoltzTraP code, we present the electron transport coefficients such as the Seebeck coefficient (S), electrical conductivity (σ), the total thermal conductivity (κ_T) which is derived from the electronic part (κ_e) and the lattice part (κ_l) of thermal conductivity, the TE power factor (PF), and finally the dimensionless TE figure of merit (ZT). For this study, we find CRTA as an advantage of the computational method since it enables more clearly the factors that generate modifications in attainable power factors for different levels of chemical substitution.⁶² The CRTA apart from being poorly reliable for metals is quite computationally efficient as calculations require only electronic band structures.⁶³ Moreover, certain methods developed for predicting the relaxation time through charge carrier scattering still possess difficulty in predicting acceptable values^{64,65} while the CRTA, although has its own limitations, accurately predicts TE properties of many compounds and is the widely used approximation.^{59,66–71} The melting point of Cu_3NbS_4 is experimentally found to be ~ 1100 K and thus we truncate our calculations at this temperature.²⁶ S , σ , and κ_e implemented in the BoltzTraP code are as given below:⁷²

$$S_{\alpha\beta}(\mu, T) = \frac{1}{eTV\sigma_{\alpha\beta}(T, \mu)} \int \bar{\sigma}_{\alpha\beta}(\mu - \varepsilon) \left[\frac{\partial f_{\mu}(T, \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \quad (14)$$

$$\sigma_{\alpha\beta}(\mu, T) = \int \bar{\sigma}_{\alpha\beta} \left[-\frac{\partial f_{\mu}(T, \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \quad (15)$$

$$\kappa_{e(\sigma\beta)}(\mu, T) = \frac{1}{e^2TV} \int \bar{\sigma}_{\alpha\beta}(\varepsilon)(\mu - \varepsilon)^2 \left[-\frac{\partial f_{\mu}(T, \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \quad (16)$$

α and β are the Cartesian indices, μ is the chemical potential, and ε and V are the energy and volume of the primitive cell respectively.

The Seebeck coefficient (S) defined by eqn (14) principally measures the induced electrical potential difference generated across the material when a temperature gradient arises. This implies that a higher $|S|$ will enhance the TE performance by generating a larger potential difference for electric current production and is inversely proportional to the temperature for a specific curve, which is observable from Fig. 6(a)–(e). The negative chemical potential illustrates p-type doping properties while n-type doping properties are illustrated by positive chemical potentials. It is observed that $|S|$ is maximum at the lowest temperature, *i.e.*, 300 K, and decreases with increasing temperature attaining the lowest at 1100 K within a particular plot. Furthermore, with this particular parameter being directly proportional to the thermoelectric figure of merit ZT , high $|S|$ is ideal for TE devices. At a particular given temperature, we observe a decrease in $|S|$ with V concentration, attaining its maximum $2745 \mu\text{V K}^{-1}$ for the Cu_3NbS_4 supercell. The diminishing $|S|$ with V substitution can be explained by the corresponding reduction of band gaps which led to an increase in carrier concentration of thermally excited charge carriers.

The resultant electrical conductivity σ obtained from eqn (15) is shown in Fig. 7(a)–(e). It should be noted that $|S|$ and σ are coupled properties, where an enhancement in one of the parameters tends to subdue the other and *vice versa*. Thus, for the same, it is indeterminate to directly predict the TE performance separately from these two parameters alone. Unlike $|S|$ which follows the systematic trend of increasing or decreasing with temperature and chemical potential, the same

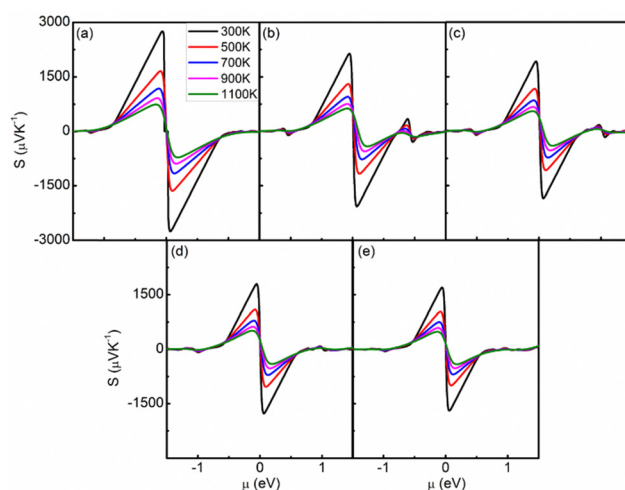


Fig. 6 Calculated Seebeck coefficient for the $\text{Cu}_3\text{Nb}_{1-X}\text{V}_X\text{S}_4$ supercell: (a) $X = 0.00$, (b) $X = 0.25$, (c) $X = 0.50$, (d) $X = 0.75$ and (e) $X = 1.00$.

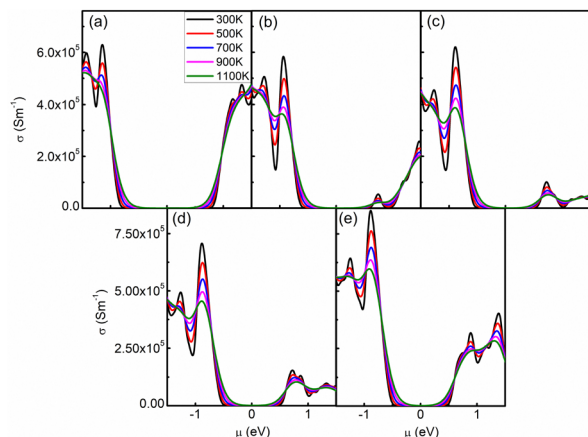


Fig. 7 Calculated electrical conductivity σ for $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$: (a) $X = 0.00$, (b) $X = 0.25$, (c) $X = 0.50$, (d) $X = 0.75$ and (e) $X = 1.00$.

cannot be derived from σ . Nonetheless, in general, our investigated SC possesses favourable σ in the order of 10^5 S m^{-1} . The conductivity first decreases for $\text{Cu}_3\text{Nb}_{0.75}\text{V}_{0.25}\text{S}_4$ as compared to the Cu_3NbS_4 supercell and then gradually increases for higher X values. Though many factors could contribute to this phenomenon, one of the straightforward reasons could be the diminishing band gaps. With reduced band gaps, charge carriers require a less amount of energy to thermally excite for inter-band transitions, effectively enhancing σ . However, a typical decline in the $\text{Cu}_3\text{Nb}_{0.75}\text{V}_{0.25}\text{S}_4$ supercell could be due to a relative decrease in the population of charge carriers in the VB near E_F as revealed from PDOS (see Fig. 3(b)).

Utilizing the resultant $|S|$ and σ , the effective TE power factor (PF) is obtained using the formula (see Fig. 8):

$$\text{PF} = S^2\sigma \quad (17)$$

The power factor PF is found to be in the moderate range, highest for the Cu_3VS_4 supercell with a decrease in magnitude under certain V/Nb concentrations and then increasing again in the Cu_3NbS_4 supercell. This trend of decreasing and

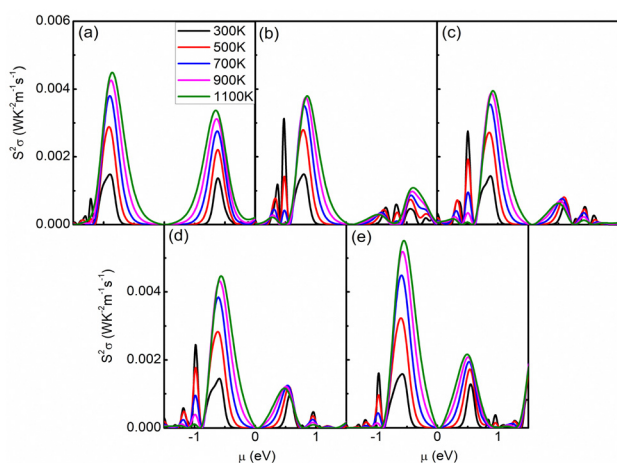


Fig. 8 Resultant power factor (PF) of the $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell: (a) $X = 0.00$, (b) $X = 0.25$, (c) $X = 0.50$, (d) $X = 0.75$, and (e) $X = 1.00$.

increasing in PF can be understood from the nature of $|S|$ and σ as discussed earlier. Also, within a particular supercell, p-type doping is relatively higher than its n-type doping counterpart indicating the p-type semiconducting nature of the SC.

In the simplest sense, thermal conductivity is a measure of how easily or difficult heat could flow through a material. Therefore, low thermal conductivity is ideal for TE devices since one has to maintain a certain temperature difference for the efficient operation of such devices. For this reason, even materials with high PF can still be rendered ineffective for TE if they possess high thermal conductivity. As already discussed in the introduction section, thermal conductivity consists of two independent components: the lattice part of thermal conductivity κ_l and the electronic part of thermal conductivity κ_e obtained using eqn (16).

$$\kappa_T = \kappa_l + \kappa_e \quad (18)$$

Here κ_T is the total thermal conductivity. The electronic part of thermal conductivity κ_e can be regarded as the thermal contribution due to the movement of charge carriers and is closely related to σ . A more definite understanding can be drawn from the κ_e plot rather than σ as its variation with temperature becomes more distinct as shown in Fig. 9. This indicates the direct proportionality of κ_e with temperature as predicted. Several methods have been used for κ_l calculations. Some employ computationally demanding calculations like ShengBTE,⁷³ first-principles Debye–Callaway⁷⁴ approach, and the high-throughput materials modelling approach especially for half-Heusler compounds.⁷⁵ Furthermore, Qin *et al.*⁷⁶ assert to have optimised the A parameter from Slack's equation, which could predict κ_l more accurately. Thus, for this current study, we employ the semi-empirical Slack's equation with the optimised A parameter according to ref. 76 as it is the most widely used for low end computational devices due to the impracticality of obtaining results from the seemingly more

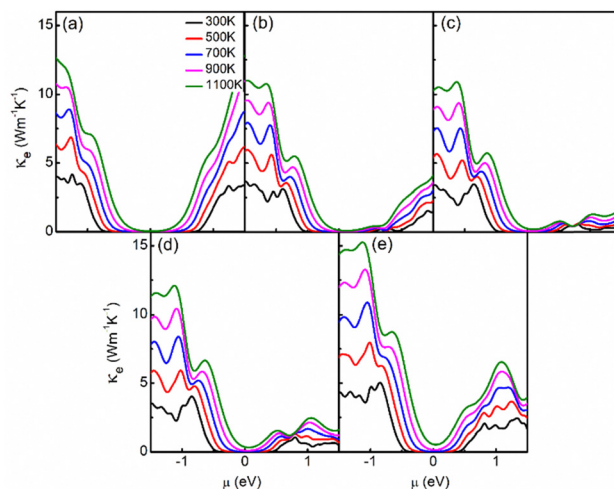


Fig. 9 Calculated electronic part of thermal conductivity for the $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell: (a) $X = 0.00$, (b) $X = 0.25$, (c) $X = 0.50$, (d) $X = 0.75$ and (e) $X = 1.00$.

accurate but computationally demanding calculations. The lattice vibration contribution towards thermal conductivity κ_l is obtained from the equation:⁷⁷

$$\kappa_l = A \frac{\bar{M} \delta \theta^3}{\gamma^2 n^{2/3} T} \quad (19)$$

where $\bar{M}$, δ , γ , n , and T are the average atomic mass, cube root of volume per atom, Grüneisen parameter, number of atoms per unit cell, and temperature respectively; the other parameters are defined in the previous sections. The optimised constant A is obtained from γ using the formula:⁷⁶

$$A = \frac{1}{1 + \frac{1}{\gamma} + \frac{8.3 \times 10^5}{\gamma^{2.4}}} \quad (20)$$

The calculated κ_l obtained from eqn (19) and (20) is shown in Fig. 10. The apparent difference between κ_l and κ_e is its inverse proportionality with temperature. Though phonon vibrations should increase with temperature, which would lead to a net increase in thermal conductivity, the contrary occurs due to Umklapp scattering, increasing the thermal resistance and leading to a net decrease in κ_l . Furthermore, κ_l can be correlated with sound velocities using eqn (7). Predicted u_m for $X = 0.00, 0.25, 0.50, 0.75$, and 1.00 are 3151, 3201, 3167, 2989, and 3055 ms^{-1} respectively. As such, κ_l also correspondingly increases or decreases with sound velocities for various X values.

Fig. 11(a) and (b) illustrates the dimensionless TE efficiency figure of merit ZT for p-type and n-type doping utilizing S , σ , κ_T , and T parameters using the formula:

$$ZT = \frac{S^2 \sigma}{\kappa_T} T \quad (21)$$

The SCs exhibit promising TE properties as observed from the figure. P-type doping exhibits higher ZT for a specific temperature than its n-type doping counterpart. At 1100 K, p-type doping reveals moderate ZT around 0.80 at all X

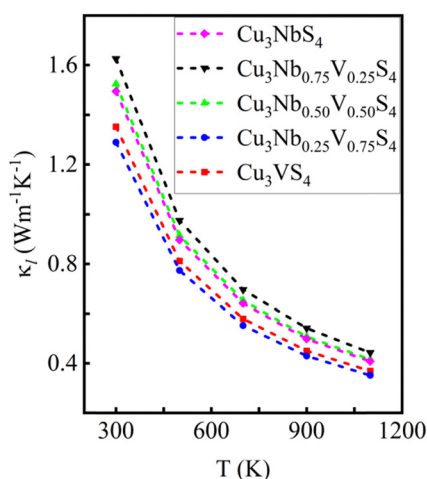


Fig. 10 Predicted lattice part of thermal conductivity for the $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell.

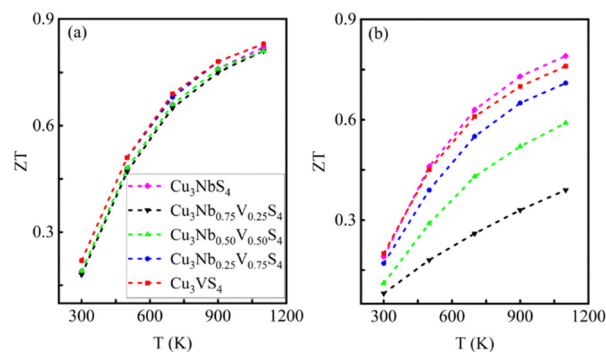


Fig. 11 Predicted maximum ZT for the $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell to temperature for: (a) p-type and (b) n-type doping.

concentrations, indicating almost independence from the X concentration whereas n-type doping exhibits diverse ZT exhibiting low values in some cases. P-type doping at all X concentrations demonstrates potential TE device application with maximum $ZT = 0.83$ for both $\text{Cu}_3\text{Nb}_{0.25}\text{V}_{0.75}\text{S}_4$ and Cu_3VS_4 at 1100 K. Though Fig. 8 demonstrates low PF for n-type doping, the unexpectedly comparable ZT with p-type doping, especially at $X = 0.00$ and 1.00 , is due to volatile deviations in κ_e resulting in the unique ZT values.

4 Conclusions

This study successfully investigates the mechanical, electronic, optical, and thermoelectric properties of a $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ ($X = 0.00, 0.25, 0.50, 0.75$, and 1.00) supercell within the DFT regime using the GGA-PBE formalism. Mechanical properties reveal the brittleness of the SCs from Poisson's as well as Pugh's ratio as an advantage over ductile materials for device fabrication. Stabilities are tested and verified from formation energy where values are consistent with already synthesized Cu_3NbS_4 , $\text{Cu}_3\text{Nb}_{0.50}\text{V}_{0.50}\text{S}_4$, and Cu_3VS_4 compounds, validating their stabilities under substitution with V. Variation of electronic properties for the $\text{Cu}_3\text{Nb}_{1-x}\text{V}_x\text{S}_4$ supercell discloses the decreasing energy band gaps in the order $X = 0.00 > 0.25 > 0.50 > 0.75 > 1.00$ with corresponding band gaps of 1.68, 1.29, 1.13, 1.08, and 1.03 eV respectively. The rationale of decreasing band gaps with V concentration has been precisely identified where Nb contributes mostly in higher energies while V has a major influence near E_F in the CB. A similar decrease in E^{opt} is observed from optical properties, indicating tunability of E^{opt} in the range of 2.11–1.53 eV. The SCs exhibit a high absorption coefficient in the order 10^5 cm^{-1} suggesting prospects for potential light absorbers especially for the $\text{Cu}_3\text{Nb}_{0.25}\text{V}_{0.75}\text{S}_4$ and Cu_3VS_4 supercell due to $E^{\text{opt}} = 1.53 \text{ eV}$, which falls close to the optimum band gaps for potential PVs. A moderate power factor of $ZT \approx 0.80$ is revealed by p-type doping with maximum values of 0.83 exhibited by $\text{Cu}_3\text{Nb}_{0.25}\text{V}_{0.75}\text{S}_4$ and Cu_3VS_4 at 1100 K. Also, the enhanced ZT and absorption coefficient in the infra-vis range with V substitution can be clarified from the relatively higher activity of V than Nb. Furthermore, due to systematic investigation into electronic properties then correlated into subsequent

related properties, this study could provide valuable theoretical insights on investigations under chemical substitution/doping in general.

Author contributions

Bernard Lalroliana – conceptualization, methodology, formal analysis, investigation, and writing the original draft. Lalmuanchhana – conceptualization, methodology, formal analysis, investigation, and software. Lalthumhima – methodology, formal analysis, investigation, and software. Diba Prakash Rai – methodology, investigation, and visualization. Lalrinthara Pachau – methodology, investigation, visualization, and conceptualization. N. Suraj-kumar Singh – methodology, investigation, visualization, and resources. Shivraj Gurung – supervision, review and editing, and resources. Lalhriatzuala – supervision, data curation, review and editing, project administration, resources, and software.

Data availability

The authors confirm that the data supporting this study are available within the article.

Conflicts of interest

The authors declare no conflicts of interest.

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Certificate

This is to Certify that

Prof./Dr./Mr./Ms. Bernard Lalroliana
Mizoram University

delivered oral/poster presentation on the topic titled

"Promising optoelectronic materials: A DFT study on Cu_3TMTe_4 (TM=V, Nb, Ta)"
at the Physical Sciences discipline technical session in the 4th Mizoram Science Congress
held at Aijal Club, Aizawl during 24-25 November, 2022

Organized by

Mizoram Science, Technology, and Innovation Council (MISTIC) in collaboration with
Mizo Academy of Sciences (MAS), Mizoram Science Society (MSS),
Science Teachers' Association, Mizoram (STAM), Geological Society of Mizoram (GSM),
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Virtual International Conference on Functional Materials & Applied Physics (FMAP-2022)

This is to certify that Mr./Mrs./Ms./Dr. Bernard Lalroliana From Mizoram University has attended & Oral presentation given in Virtual International Conference on Functional Materials & Applied Physics (FMAP-2022) under Center for Continuing Education (CCE), Organized by Department of Physics, Sardar Vallabhbhai National Institute of Technology, Surat, during 14-15 October, 2022.

**Dr. Yogesh Sonvane
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SRM INSTITUTE OF SCIENCE AND TECHNOLOGY

Kattankulathur - 603 203, Tamil Nadu, India.

7th International Conference on Nanoscience and Nanotechnology (ICONN-2023) (Virtual Conference) March 27 - 29, 2023

Certificate of Participation

This is to certify that Mr. / Ms. / Dr. **Bernard Lalroliana** has participated and presented a paper entitled **Theoretical modeling of copper sylvanite Cu_3TaTe_4 [100] surface: Electronic and magnetic properties** in the 7th International Conference on Nanoscience and Nanotechnology (ICONN-2023) organized by Department of Physics and Nanotechnology, SRM IST, India during March 27- 29, 2023, in association with Shizuoka University, Japan; National Yang Ming Chiao Tung University, Taiwan; GNS Science, New Zealand; University of Rome Tor Vergata, Italy; Asian Consortium on Computational Materials Science (ACCMS), Japan; Indian Ceramic Society; Indian Physics Association (IPA); Solar Energy Society of India (SESI); Innovation, Science & Technology Foundation - Tirupati (ISTF-T) and co-sponsored by Defence Research and Development Organization (DRDO), India; Council of Scientific & Industrial Research (CSIR), India; The Indian Science Congress Association (ISCA) and Springer Nature.

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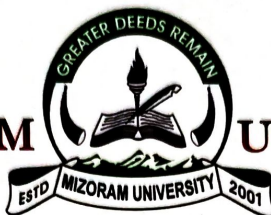
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MIZORAM UNIVERSITY



A CENTRAL UNIVERSITY ESTABLISHED BY AN ACT OF PARLIAMENT, ACCREDITED 'A' GRADE BY NAAC (2019)

Certificate of Presentation

This certificate acknowledges that

Mr./Ms./Dr. Bernard Lalroliana
Department of Physics, Mizoram University

has successfully presented the paper entitled "Theoretical Insights of Electronic Properties of Nb-Doped Cu₃VS₄" at the International Conference on Recent Advances in Mathematical, Physical, and Chemical Sciences (ICRAMPC-2024) organized by School of Physical Sciences, Mizoram University, Aizawl during February 21-23, 2024.

Prof. Dibakar Chandra Deka
Vice-Chancellor

Prof. Suman Rai
Dean & Chairman

Prof N. Mohandas Singh
Convener

CERTIFICATE

THIS IS TO CERTIFIED THAT

Bernard Lalroliana

delivered oral presentation on the topic titled,
“Enhanced property under V doped on Nb Sites
for Cu_3NbS_4 ”

at the International Conference

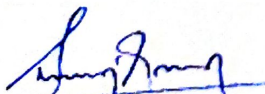
on

“Exploring the complexities of Physical and Earth System dynamics through
modeling and data analysis” held at Seminar Hall, Pachhunga University
College, Aizawl during 27 - 29 Feb, 2024

Organized by

School of Physical Science, Pachhunga University College




PROF. SHIVRAJ GURUNG
CHAIRMAN


PROF. H. LALTHANZARA
PATRON

PARTICULARS OF THE CANDIDATE

NAME OF THE CANDIDATE : BERNARD LALROLIANA

DEGREE : DOCTOR OF PHILOSOPHY

DEPARTMENT : PHYSICS

TITLE OF THESIS : AN AB INITIO INVESTIGATION OF
COPPER SULVANITES: BULK AND
LAYERED NANO STRUCTURE

DATE OF ADMISSION : 13.09.2021

APPROVAL OF RESEARCH PROPOSAL

1. DRC : 22.03.2022

2. BOS : 08.04.2022

3. SCHOOL BOARD : 07.06.2022

4. MZU REGISTRATION No. : 2107645

5. Ph.D. REGISTRATION No. : MZU/Ph.D./1865 of 13.09.2021

6. EXTENSION IF ANY : NIL

(Prof. B. Lalremruata)

Head

Department of Physics

ABSTRACT

AN AB INITIO INVESTIGATION OF COPPER SULFANITES: BULK AND LAYERED NANO STRUCTURE

**AN ABSTRACT SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY**

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MZU REGISTRATION NO.: 2107645

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**DEPARTMENT OF PHYSICS
SCHOOL OF PHYSICAL SCIENCES
AUGUST, 2025**

**AN AB INITIO INVESTIGATION OF COPPER SULFANITES: BULK AND
LAYERED NANO STRUCTURE**

By

BERNARD LALROLIANA

DEPARTMENT OF PHYSICS

Supervisor

Prof. LALHRIATZUALA

Joint Supervisor

Prof. SHIVRAJ GURUNG

Submitted

**In partial fulfillment for the requirement of the Degree of Doctor of Philosophy
in Physics of Mizoram University, Aizawl**

THESIS TITLE: An *ab initio* investigation of copper sylvanites: Bulk and layered nano structure

Introduction

We have successfully investigated the bulk, doped, and surface slab properties of the compound from theoretical insights along with their application prospects, where our study result outlines new findings due to our novel research approach as compared to the numerous existing literatures. Also, just as our research puts its main emphasis on the photovoltaic and thermoelectric prospects for green energy harvesting, our results put more stress on these properties from both the bulk and doped structures, while basic properties are explored in surface slab models due to their non semiconducting nature. The following below are the conclusions we have drawn from our study:

Chapter 1: Contains the introduction of the present studies of copper sylvanite compounds, including the literature review of the respective compounds stressing on the energy prospects. It also contains the brief introduction on the DFT approach of absorber layer for photovoltaics and working principle of the Seebeck effect in thermoelectric device.

Chapter 2: This chapter covers description of the tools for the proposed studies, containing concise description of the methodology including DFT and how the structural, mechanical, electronic, thermoelectric, etc and other properties are studied using the DFT techniques employing the Hubbard correction as implemented by certain software.

Chapter 3: This chapter encompasses the mechanical, electronic, dynamical stability, optical, and thermoelectric properties of Cu_3NbX_4 ($\text{X}=\text{S}, \text{Se}, \text{Te}$) at 0, 5, 10, 15, and 20 GPa isotropic pressure within the framework of DFT+U with the incorporation of SOC. The calculated results are found in good agreement with experimental data, specifically in lattice parameters and optical band gaps. Comparable optical band gaps with experiments are especially an advantage as

accurate prediction of electronic dependant properties greatly rely on it. Cu_3NbX_4 exhibits promising optical properties for photovoltaic applications with enhanced properties under pressure. Transport properties are obtained from the BolzTraP code that follows the Boltzmann transport equation. Instead of utilizing the CRTA, relaxation time is calculated for each compound and under pressure from the deformation potential theory. Moderate thermoelectric efficiency with slight improvement under pressure is observed.

Chapter 4: This chapter contains the study result of mechanical, energetical stability, electronic, optical, and thermoelectric properties of Copper Sulvanites $\text{Cu}_3\text{Nb}_{x-1}\text{V}_x\text{S}_4$ ($x=0.00, 0.25, 0.50, 0.75, 1.00$), doped with V on Nb site using the GGA-PBE approximation. Energetical stabilities are verified from formation energies. Further, enhanced optical and thermoelectric properties are observed in this doping investigation.

Chapter 5: Surface slabs derived from the bulk Cu_3TaTe_4 are investigated in this section. Full metallic character and half metallic characters are observed from the four symmetric surface terminals unlike the semiconducting character in their bulk states. Structural, energetical stability from formation energy, and electronic properties are investigated. Further, surface reconstruction is observed in one of the terminals which probably enhanced its stability.

Chapter 6: This chapter contains the resultant outcome of the study as a whole especially where photovoltaic absorber prospects is identified for certain pressure and doping.