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STUDY OF THE PHYSICAL PROPERTIES OF PEROVSKITES BASED ON CHALCOGENIDES FOR PHOTOVOLTAIC APPLICATIONS

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Dedication

I dedicate this work to every member of my family, especially my parents, who profoundly shaped my scientific ethics from an early age and continuously supported me throughout my journey. I also extend my gratitude to my sisters and my brother for their unwavering support.

To all those who contributed, directly or indirectly, to the completion of this work.

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Abstract

This thesis explores chalcogenide-based perovskites, which offer several advantages and show high potential for use in solar cells and optoelectronic technologies. Due to their exceptional band gaps and outstanding light-absorption capabilities, they are especially suitable for these applications. Using the Full-Potential Linearized Augmented Plane Wave (FP-LAPW) method within the framework of Density Functional Theory (DFT), this study aimed to evaluate the structural, elastic, electronic, optical, and thermoelectric properties of CaSiX_3 systems with partial atomic substitutions ($X = \text{S}, \text{Se}, \text{or Te}$). The orthorhombic phase of these chalcogenides is confirmed to be both structurally and thermodynamically stable, as evidenced by optimized structural parameters and negative formation energies. Mechanical analysis shows that CaSiSe_3 and CaSiTe_3 are ductile, while CaSiS_3 is brittle, as indicated by their Pugh and Poisson ratios. The electronic band structure calculations reveal band gaps energy of 3.02 eV for CaSiS_3 and 1.71 eV for CaSiSe_3 , indicating that CaSiS_3 is suitable for UV-light absorption and PV, while CaSiSe_3 exhibits absorption in the visible red and near-infrared regions. Conversely, CaSiTe_3 exhibits metallic behavior. Optical properties, such as the complex dielectric function and absorption coefficients, indicate strong ultraviolet absorption, further supporting their use in optoelectronic ultraviolet and PV applications. The AMPS-1D (Analysis of Microelectronic and Photonic Structures-One Dimensional) package was used to evaluate the solar cell efficiency, confirming their suitability for photovoltaic systems. Additionally, BoltzTrap2 was used to analyze thermoelectric properties at various temperatures, revealing figure-of-merit (ZT) values of 0.47 for CaSiS_3 and 0.40 for CaSiSe_3 . While capable of combining solar and thermoelectric functions, these values highlight their potential for integration into renewable energy systems.

Keywords: Chalcogenides, FP-LAPW, DFT, Perovskites, light absorption, AMPS-1D, solar cell.

Résumé

Cette thèse explore les chalcogénures, qui présentent plusieurs avantages et un fort potentiel pour les cellules solaires et les technologies optoélectroniques. Grâce à leur large bande interdite et à leurs excellentes capacités d'absorption de la lumière, ils sont particulièrement adaptés à ces applications. Utilisant la méthode des ondes planes augmentées linéarisées à potentiel complet (FP-LAPW), dans le cadre de la théorie de la fonctionnelle de la densité (DFT), cette étude a évalué les propriétés structurales, élastiques, électroniques, optiques et thermoélectriques des systèmes CaSiX_3 , avec des substitutions atomiques partielles ($X = \text{S}, \text{Se}$ ou Te). La phase orthorhombique de ces chalcogénures est confirmée comme étant à la fois structurale et thermodynamiquement stable, comme en témoignent l'amélioration des paramètres structuraux et les énergies de formation négatives. Les calculs de la structure électronique des bandes révèlent des énergies de bande interdite de 3.02 eV pour le CaSiS_3 et de 1.71 eV pour le CaSiSe_3 , indiquant que le CaSiS_3 est adapté à l'absorption de la lumière UV et aux applications photovoltaïques, tandis que le CaSiSe_3 présente une absorption dans les régions du visible rouge et du proche infrarouge. À l'inverse, CaSiTe_3 présente un comportement métallique. Les propriétés optiques, telles que la fonction diélectrique complexe et les coefficients d'absorption, indiquent une forte absorption dans les applications optoélectroniques ultraviolettes et photovoltaïques., ce qui confirme leur utilisation dans les applications solaires. Le programme AMPS-1D (Analyse des structures microélectroniques et photoniques unidimensionnelles) a été utilisé pour évaluer le rendement des cellules solaires, confirmant leur aptitude à être intégrées dans les systèmes photovoltaïques. De plus, BoltzTrap2 a permis d'analyser les propriétés thermoélectriques à différentes températures, révélant des facteurs de mérite (ZT) de 0,47 pour CaSiS_3 et de 0,40 pour CaSiSe_3 . Capables de combiner des fonctions solaires et thermoélectriques, ces valeurs soulignent leur potentiel d'intégration dans les systèmes d'énergie renouvelable.

Mots-clés : Chalcogénures, FP-LAPW, DFT, Pérovskites, absorption de la lumière, AMPS-1D, cellule solaire.

ملخص

تستكشف هذه الأطروحة الكالكوجينيدات، التي توفر مزايا عديدة وإمكانات هائلة للخلايا الشمسية وتقنيات الإلكترونيات البصرية. بفضل فجوة نطاقها الواسعة وقدراتها الممتازة على امتصاص الضوء، فهي مناسبة بشكل خاص لهذه التطبيقات. باستخدام طريقة الموجة المستوية المعززة الخطية ذات الجهد الكامل (FP-LAPW) في إطار نظرية الكثافة الوظيفية (DFT)، قُيِّمت هذه الدراسة الخصائص البنيوية، المرنة، الإلكترونية، البصرية، والحرارية الكهربائية لأنظمة CaSiX_3 ذات الاستبدالات الذرية الجزئية ($\text{X} = \text{S}, \text{Se}, \text{أو Te}$). وقد تأكد أن الطور المعيني القائم لهذه الكالكوجينيدات مستقر بنيويًا وديناميكيًا حراريًا، كما يتضح من تحسن المعاملات البنيوية وطاقات التكوين السالبة. يُظهر التحليل الميكانيكي أن CaSiSe_3 و CaSiTe_3 يتميزان بالليونة، بينما CaSiS_3 هش، كما هو موضح من خلال معاملات بوغ وبواسون الخاصة بهما. تكشف حسابات بنية النطاقات الإلكترونية عن طاقات نطاق محظور تبلغ 3.02 إلكترون فولت لـ CaSiS_3 و 1.71 إلكترون فولت لـ CaSiSe_3 ، مما يشير إلى أن CaSiS_3 الأشعة فوق البنفسجية وتطبيقات الخلايا الكهروضوئية، في حين أن CaSiSe_3 يمتص الضوء في نطاقي الضوء المرئي والأشعة فوق البنفسجية. على العكس من ذلك، يُظهر CaSiTe_3 سلوكًا معدنيًا. تشير الخصائص البصرية، مثل الدالة العازلة المعقدة ومعاملات الامتصاص، إلى امتصاص قوي للأشعة فوق البنفسجية، مما يؤكد ملاءمتها للاستخدام في تطبيقات الطاقة الشمسية. استُخدم برنامج AMPS-1D (تحليل الهياكل الإلكترونية الدقيقة والفوتونية أحادية البعد) لتقييم كفاءة الخلايا الشمسية، مما يؤكد ملاءمتها للدمج في أنظمة الطاقة الكهروضوئية. علاوة على ذلك، مكن BoltzTrap2 من تحليل الخصائص الكهروحرارية عند درجات حرارة مختلفة، كاشفًا عن قيم الجدارة (ZT) البالغة 0.47 لـ CaSiS_3 و 0.40 لـ CaSiSe_3 . بفضل قدرتها على الجمع بين الطاقة الشمسية والحرارية الكهروحرارية، تُبرز هذه القيم إمكانية دمجها في أنظمة الطاقة المتجددة.

الكلمات المفتاحية: الكالكوجينيدات، FP-LAPW، DFT، البيروفسكايت، امتصاص الضوء، AMPS-1D، الخلية الشمسية.

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General introduction

The study of semiconductor materials has a long history dating back to the 19th century, when *M. Faraday* observed that increased temperature was associated with enhanced conductivity, leading to the identification of these materials as semiconductors. Both organic and inorganic halide perovskites have grown in importance in this field in recent years. Their outstanding results and swift advances in solar technology have been impressive. This category of materials describes a broader range of naturally occurring compounds, the first of which, CaTiO_3 , was discovered by *Gustav Rose*. Consequently, perovskite materials (structures) were named in honor of *Lev Perovski* [1]. Extensive research has been conducted on perovskite materials and their derivatives, with particular emphasis on their structural, chemical, and physical properties [2].

These materials are not limited to cubic, tetragonal, and monoclinic structures. The orthorhombic structure is particularly significant due to its unique features. The scientific community has recently focused on chalcogenide perovskites, which have attracted greater interest in recent years. Chalcogenide perovskites exhibit remarkable optoelectronic characteristics and low toxicity, and they can also be manufactured with great precision using molecular beam epitaxy [3]. Halide perovskites such as NaGeX_3 [4], TlGeX_3 [5], CsGeX_3 [6], AGeF_3 [7], and TlSnX_3 [8] exemplify systems in which the tetravalent oxidation state is the most stable.

The search for advanced materials for the development of next-generation photovoltaic (PV) technologies has re-ignited as the global need for sustainable and clean energy increases. Scientists have made significant efforts to harvest and convert solar energy into useful forms due to its established status as the cleanest and most sustainable energy source [9]. Chalcogenide-based perovskites represent a highly promising family of materials with applications in energy storage and optoelectronics. Chalcogenide-based perovskites offer unique advantages, such as increased stability, non-toxicity, and broader bandgap tunability. In contrast to conventional semiconductor materials commonly used as absorption layers in solar cells, chalcogenide-based perovskites exhibit exceptional optical and electrical properties, making them strong candidates for future photovoltaic technologies.

Perovskite materials can be synthesized using various methods. The most commonly used technique is solution deposition [10], which involves dissolving both organic and inorganic materials in an appropriate solvent. These materials are then sprayed or coated onto a surface to form uniform layers. The layers undergo heat treatment and drying to enhance the film's quality

and crystallinity. These procedures are scalable and cost-effective to meet the requirements of various applications, including sensors and solar cells [11].

Chalcogenide-based perovskites could be the next generation of high-performance semiconductors [3,12]. Chalcogenide perovskites have physical properties similar to those of oxide perovskites, including high dielectric polarization, and possess a bandgap (E_g) in the visible and near-infrared (VIS-NIR) bands [12–15]. In addition, they are known for their excellent thermal and chemical stability, making them superior in many applications. Furthermore, these materials are characterized by safe, non-toxic raw materials that are widely available in nature, reinforcing their economic and productive viability. This makes them an ideal choice for many sustainable industrial and technological applications. Findings show that replacing oxygen (O) with either sulfur (S) or selenium (Se) reduces the bandgap, making them suitable for solar cell applications [16]. A theoretical review of 18 chalcogenide-based ABX_3 ($A = \text{Ca/Sr/Ba}$, $B = \text{Ti/Zr/Hf}$ and $X = \text{S/Se}$) for photovoltaic applications has been carried out [13]. The successful synthesis of chalcogenide-based perovskites, which exhibit remarkable properties, has recently been supported by various theoretical and experimental investigations [14,17–20]. A series of recent experimental investigations has been conducted on a number of chalcogenide-based perovskites, including BaZrS_3 , BaTiS_3 , SrZrS_3 , SrTiS_3 , CaZrS_3 , and CaSnS_3 [17,19,21,22].

This work is a study of the structural, elastic, electronic, optical, thermoelectric, and thermodynamic properties of CaSiX_3 ($X = \text{S, Se, and Te}$), which crystallize in the orthorhombic structure with a Pnma ($N^\circ 62$) space group, using density functional theory (DFT) implemented in the WIEN2k code [23–26]. The analysis begins with determining the ground state parameters, especially the bulk modulus and lattice parameters. Using relaxed structural parameters ensures the stability of the structure, as shown by the calculated elastic constants and the negative formation energy. The phonon frequency spectra also support the stability findings from the PBE-GGA method [27]. The electronic properties display semiconductor behavior, with favorable optical features and significant thermoelectric performance based on the TB-mBJ approach [27].

The work presented in this thesis is broken up into four chapters:

- The first chapter provides a literature review of perovskites, placing special emphasis on chalcogenide perovskites, including their structure and classifications.

- In Chapter II, we discuss the applications and manufacturing process of photovoltaic solar cells.
- Chapter III presents the results obtained in this study using the Density Function Theory (DFT), implemented through the wien2k software for the compounds under investigation. Structural and crystalline properties are analyzed using the PBE-GGA method, these calculations highlight the overall performance of the compounds, confirming their structural stability and application potential. while the electronic, optical and thermal properties are examined using the modified Tran-Blaha modified Becke-Johnson (TB-mBJ) approximation.
- In Chapter IV, we used WxAMPS-1D to evaluate the performance of two proposed solar cell architectures based on the results from chapter III.



Chapter I: Overview on the perovskite materials

I.1. Introduction

The term 'perovskite' was primarily attributed to the mineral calcium titanium oxide (CaTiO_3). (*L. A. Perovski 1839*) [28].

'Perovskite' now refers to a class of compounds that share the same ABX_3 atomic structure. In this structure, 'A' stands for the largest cation, 'B' for the smaller cation, and 'X' for the anion. The anion component can include oxides [29], fluorides [30], hydrides [31].

The perovskite structure is widely studied in materials science due to its prevalence and valuable properties, including high thermopower, ferroelectricity, and superconductivity. [32].

I.2. ABX_3 perovskite

The Perovskite structures have attracted significant interest for a variety of technological applications during the past few decades. Their structural advantages and tunable physico-chemical characteristics have been extensively studied. *Fig. I.1* shows the crystal structure of a perovskite with the formula ABO_3 [33]. This term encompasses a group of compounds with a shared atomic structure: the 'A' cation, the largest, occupies the body center site; the 'B' cation, smaller, occupies the corner positions; and the 'O' anions are located at the cubic lattice centers (see *Fig. I.1*). Many materials with ABX_3 composition exhibit this same crystal structure [34]. Because cation (A and B) substitutions are flexible, researchers can modify perovskite properties to suit specific applications.

As ideal examples of phase transitions, these materials exhibit readily accessible cubic, tetragonal, orthorhombic, trigonal, and monoclinic polymorphs, which are determined by the degree of tilting and rotation of the BX_6 octahedra in the lattice [34–37]. Various factors can result in octahedral distortion in perovskite materials. One explanation for octahedral distortion in perovskite materials is the difference in radius between the A and B cations. One cation may distort in the nearby octahedra to accommodate its size if the others are too big to fit comfortably inside the lattice's octahedral gaps due to their vastly differing sizes [38].

Each atom in perovskite compounds can occupy a wide range of configurations, as seen in *Fig. I.1*. Due to their adaptable crystal structure, these compounds allow atoms to be arranged differently based on their chemical composition and environmental factors. There are many

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possible positions for oxygen. The figure depicts the various possible positions for oxygen, B-site, and A-site atoms within the perovskite lattice. Many versions of the perovskite structure, each with distinct features and uses, can be formed due to this flexibility in atomic placement. Perovskites can be categorized by cell structure, which helps to understand their many features and possible uses.

Various studies have identified several of the perovskite structures with potential for technological applications. These structures include orthorhombic [39], rhombohedral [40], tetragonal [41], and even hexagonal [42] forms. One practical way to learn more about the structural features that influence the physical, chemical, and performance-related behaviour of perovskite compounds is to observe the arrangement of atoms in the crystal lattice, including changes in symmetry and distortions of the oxygen octahedra.

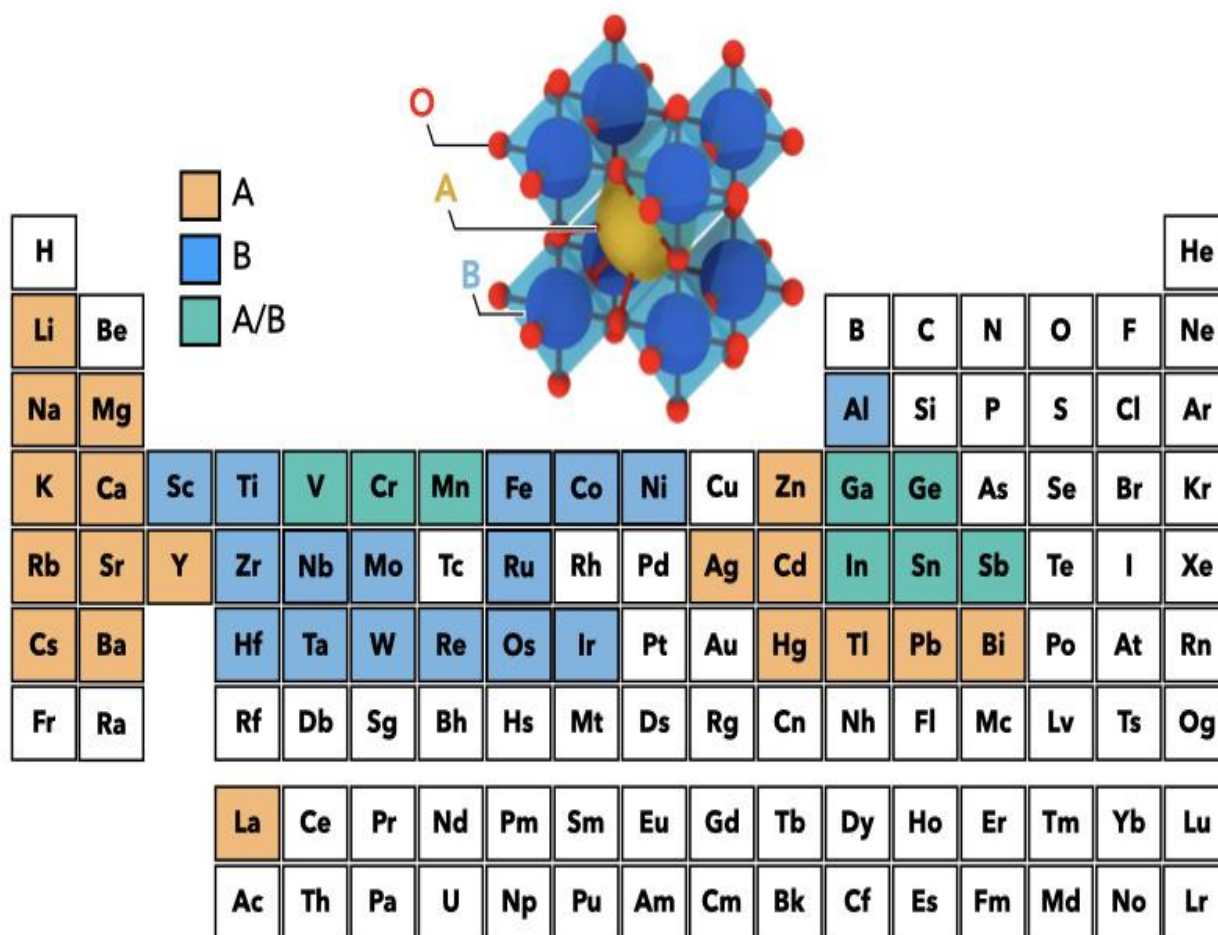


Fig. I.1: Perovskite unit cell configuration [33].

1.2.1. Monoclinic and triclinic phases in perovskite structures

The existence of both triclinic structures (such as BeFeO_3 [43], BiCrO_3 [44], CuAgF_3 [45], PbSnO_3 [46], and PbCrO_3 [47]) and monoclinic structures (such as BiScO_3 , MnBiO_3 [48] and NdMnO_3 [49]) has been reported in several previous studies.. These structures can transform into stable phases under specific chemical or physical conditions, such as epitaxial strain, high pressure, or customized cation ordering, even though they are often considered metastable or prone to distortion under ambient conditions [50]. We can take MnBiO_3 (monoclinic, $P2_1/c$) and CuAgF_3 (Triclinic, $P\bar{1}$) as a simple example with $\alpha \neq \beta \neq \gamma \neq 90^\circ$, and Manganese/Copper ions are present at the A sites of the ABO_3 structure. Still, the B sites can contain Bismuth/Silver ions, both have a ratio of 1:1 as shown in [Fig. I.2](#). These phases are frequently stable because of cooperative distortions that suppress higher-symmetry alternatives and decrease the overall energy, such as lone-pair-driven off-centring (e.g., Bi^{3+} 6s² electrons) or octahedral tilting ($a^-b^+c^-$ in Glazer notation).

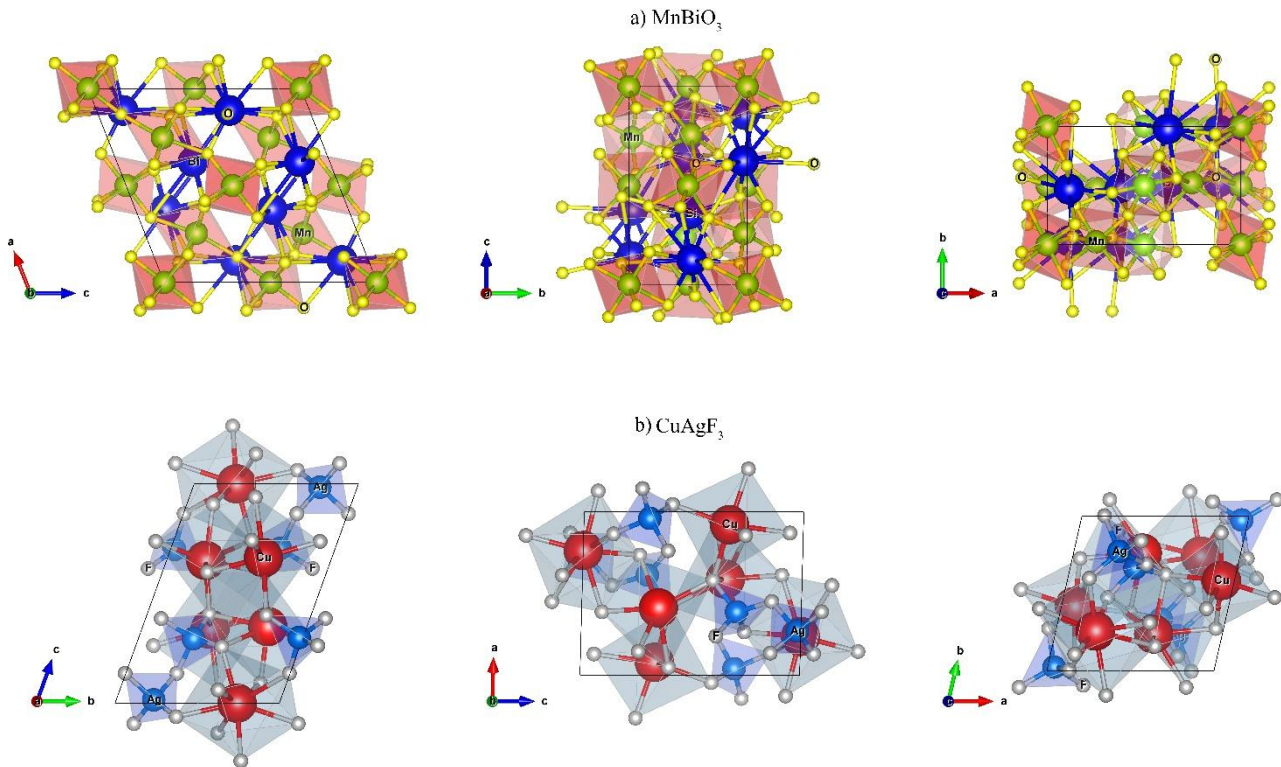


Fig. I.2: Monoclinic perovskite structure of MnBiO_3 (a) and CuAgF_3 (b).

1.2.2. Orthorhombic perovskite

Recent studies have more accurately determined the structure of some perovskites. These studies provide a basis for subsequent modelling of the semiconducting properties, which are a key characteristic of this perovskite structure, making it a popular choice for photovoltaic applications, due to its superior properties. The geometrical ground state at the (Pbnm/62, $\alpha = \beta = \gamma = 90^\circ$) space group for this type of structure is presented in [Fig. I.3](#) with a multi-sided view. We can recognise many compounds with this design, such as the CaSnO_3 [51], GdFeO_3 [52], and SrRuO_3 [53]. The BaZrSe_3 structure is highly indicative of an orthorhombic perovskite structure. Its space group is Pnma, characterised by the lattice parameters $a = 4.0808 \text{ \AA}$, $b = 9.1520 \text{ \AA}$, and $c = 15.1479 \text{ \AA}$ [54].

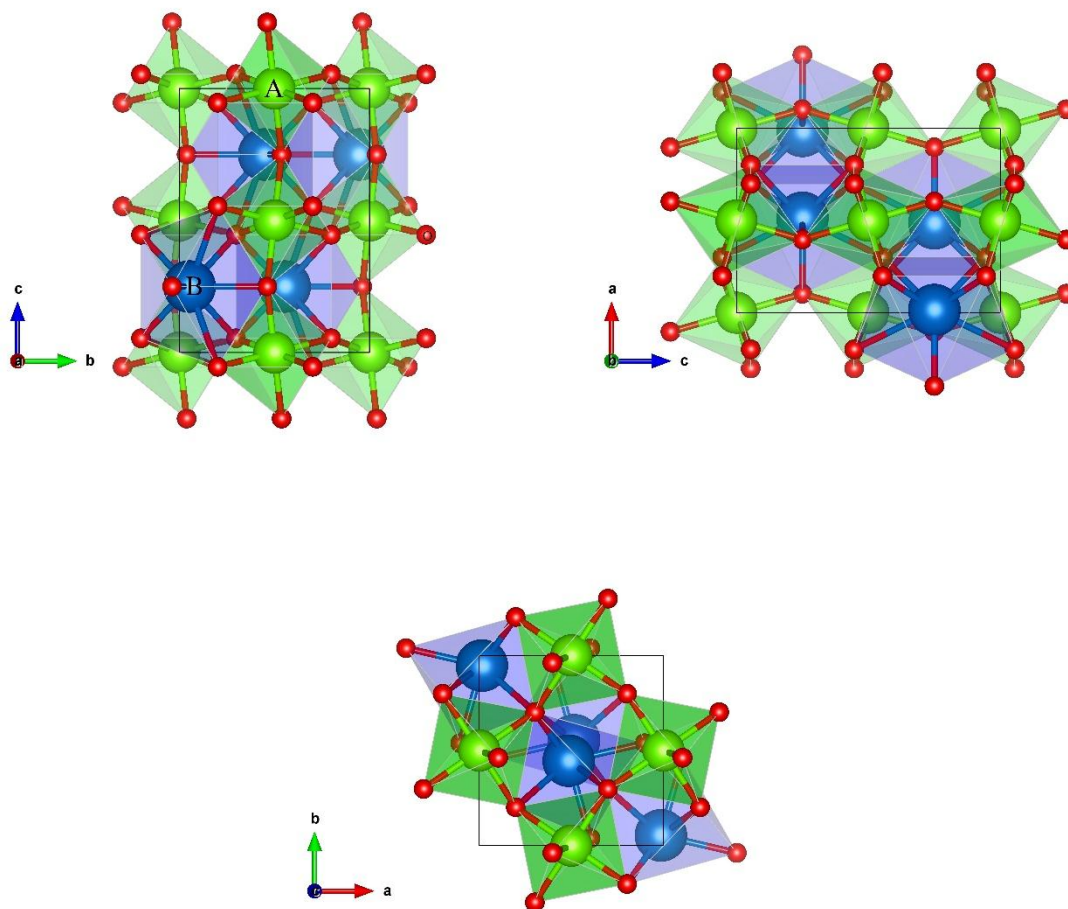


Fig. I.3: Orthorhombic (Pnma) crystal structure of ABO_3 .

1.2.3. Tetragonal perovskite structure

The perovskite structure can be formed by various oxides with the chemical formula ABO_3 , and the tetragonal structure is one of them (*Fig. I.4*). Although tetragonal structures (space groups $I4/mcm$ or $P4mm$) are also viable, cubic structures are the preferred form for perovskite materials. Among the most studied materials in perovskites is $BaTiO_3$ with $a = 3.979 \text{ \AA}$, and $c = 4.078 \text{ \AA}$ in the tetragonal case ($\alpha = \beta = \gamma = 90^\circ$) [29].

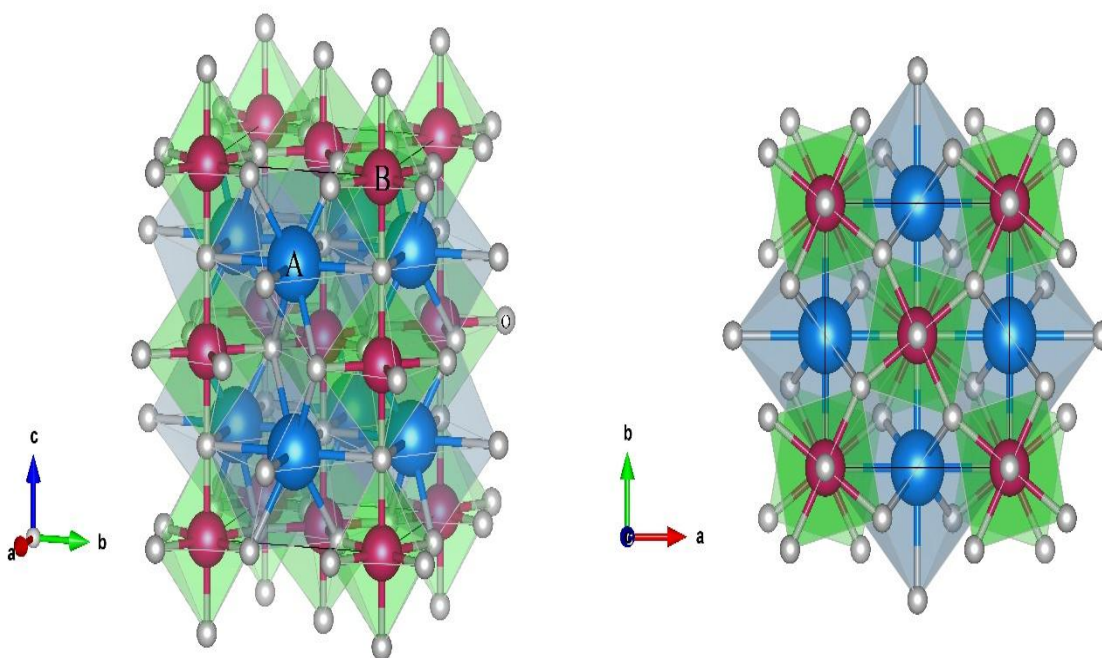


Fig. I.4: stable tetragonal ($I4/mcm$) configuration for ABO_3 perovskites.

1.2.4. Rhombohedral perovskite

Three parameters, a , b , and c , and three angles that are equal but not 90° define a rhombohedron structure. Instances of this structure include $SmAlO_3$, which belongs to the $\bar{R} 3m$ space group, with $a = 5.316 \text{ \AA}$ and an angle of 60.19° [55]. $LaCoO_3$, or lanthanum cobaltate, is a perovskite oxide with a rhombohedral crystal structure, with $a = 5.3416 \text{ \AA}$ and an angle of 60.99° [56].

Rhombohedral perovskites are increasingly recognized as a diverse category of ceramics. Notably, ceramics like $LaAlO_3$ and $PrAlO_3$ [57] play an important role in recent research on lattice

Chapter I: Overview on the perovskite materials

dynamics. Rhombohedral perovskites are well-suited for technological applications, with functionality significantly influenced by the tilt distortions present in these structures.

1.3. Stability conditions for a perovskite structure

The stability of the perovskite structure is primarily determined by two key parameters: the tolerance factor and the octahedral factor.

1.3.1. Tolerance factor

The first idea for the tolerance factor " t " was proposed by Megaw [58] to evaluate the stability of the perovskite phase for certain anions and cations. The unit cell length (a) in an ideal cubic perovskite structure is proportional to the ionic radii as follows [59]:

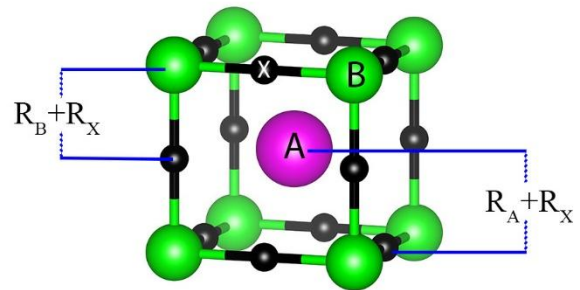
$$a = \sqrt{2}(R_A + R_X) = 2(R_B + R_X) \quad (I.1)$$

R_A , R_B , and R_X are the ionic radii of the A and B cations and the X anion. Based on purely geometrical considerations, it is possible to predict both the stability and formability of a particular perovskite structure by using the ionic radii of the atoms in its composition to calculate the Goldschmidt tolerance factor (t) [60,61], which is expressed as:

$$t = \frac{(R_A + R_X)}{\sqrt{2} (R_B + R_X)} \quad (I.2)$$

This factor describes how well the two subsystems, "AX" and "BX", are matched. The structure is only possible within the range of $0.8 \leq t \leq 1.08$; thus, the ion radius of cation A is always larger than that of cation B. Perfect compact stacking occurs when $t = 1$. Cation B may be mobile inside the system for $t > 1$. The A cation is the one that can move around the system when $t < 1$. The closer t gets to 1, the more stable the perovskite phase becomes. Many elements can combine to generate distorted perovskite structures for either lower or larger values of t .

Due to the different degrees of distortion, perovskite structures can be loosely classified in the following way: (i) Orthorhombic, with the highest distortion and lowest symmetry,



characterized by a tolerance factor $t < 0.87$ (e.g., CaTiO_3 , GdFeO_3); (ii) Tetragonal with less distortion and a higher tolerance factor in the range of $0.81 < t < 0.87$; (iii) Cubic, which is expected to be stable in the range of $0.89 < t < 1$ (e.g. SrTiO_3 , BaTiO_3) [60–64], and (iv) Hexagonal, which occurs for $t > 1$ (e.g. BaNiO_3) [63]. The following table shows how different situations can be differentiated based on the value of the tolerance factor.

Table I.1: The tolerance factor (t) for crystal structures [65].

<i>Cubic</i> $0.89 < t < 1.05$	<i>Tetragonal</i> $0.97 < t < 1$	<i>Hexagonal</i> $t > 1.05$
<i>Orthorhombic or monoclinic</i> $t < 0.97$	<i>Ilmenite</i> $t < 0.76$	

I.3.2. Stability analysis of anion-cation bonds

To determine the stability of a perovskite structure, it is crucial to consider the ionicity of the anion-cation bond. The difference in electronegativity between the ions in an ABO_3 perovskite structure can provide valuable insights into its stability. Enhanced thermal stability in perovskite structures is achieved through the pronounced ionic character of both cation-anion bonds [66]. The ionicity of bonds can be calculated using the following formula:

$$\bar{x} = \frac{x_{A-O} + x_{B-O}}{2} \quad (I.3)$$

Where $A-O$ and $B-O$ stand for the variations in electronegativity between the cations (A and B) and the oxygen anions that are connected with them. Perovskite possesses bonds that exhibit both ionic and non-negligible covalent characteristics. Changes in the A-site cation can influence the nature of the B-O bond [67,68]. For example, in Ca_2MnWO_6 , the Mn-O bond is longer than in Sr_2MnWO_6 due to the lower electronegativity of Ca relative to Sr, which weakens the Mn-O bond [69].

I.4. Double perovskite

Perovskite oxides are among the most researched compounds in solid-state chemistry because they are extraordinarily capable of displaying several structural changes and include a wide range of elemental compositions. Ward and Galasso first reported their discovery in the early 1960s, further highlighting the intriguing diversity and complexity of double perovskite compounds [70,71].

1.4.1. Structural insights into $A_2BB'X_6$ double perovskites

Double perovskites, denoted by the formula $A_2BB'X_6$ (**Fig. 1.5**), enhance the flexibility of traditional perovskite structures (ABX_3) by integrating two distinct cations (B and B') in a rock-salt configuration [72–74]. This architectural adjustment opens up a broad spectrum of compositional possibilities and enables the customization of material properties for specialised uses. Generally, the A site hosts a single-valence cation, such as caesium (Cs) or a larger organic cation, while the X site accommodates an anion, often a halide such as chloride (Cl), bromide (Br), or iodide (I). Altering the B-site cations introduces a vast potential for adjusting electronic, optical, and thermal characteristics [70].

The double and simple perovskites exhibit notable differences in structural, compositional, and property characteristics. Within this structure, the A cation with coordination number 12 occupies the centre of the cuboctahedron. The two transition metals alternately occupy the B sites with coordination number 6, each surrounded by oxide anions, forming BO_6 and $B'O_6$ octahedra, which are joined at their vertices [75].

Simple perovskites feature a single B-site cation within a framework of corner-sharing BX_6 octahedra, often exhibiting high symmetry such as cubic or minimally distorted forms. Conversely, double perovskites incorporate two distinct B-site cations (B and B') in an ordered rock-salt configuration. This results in a more intricate lattice structure and generally lower symmetry, often in tetragonal or monoclinic forms [76].

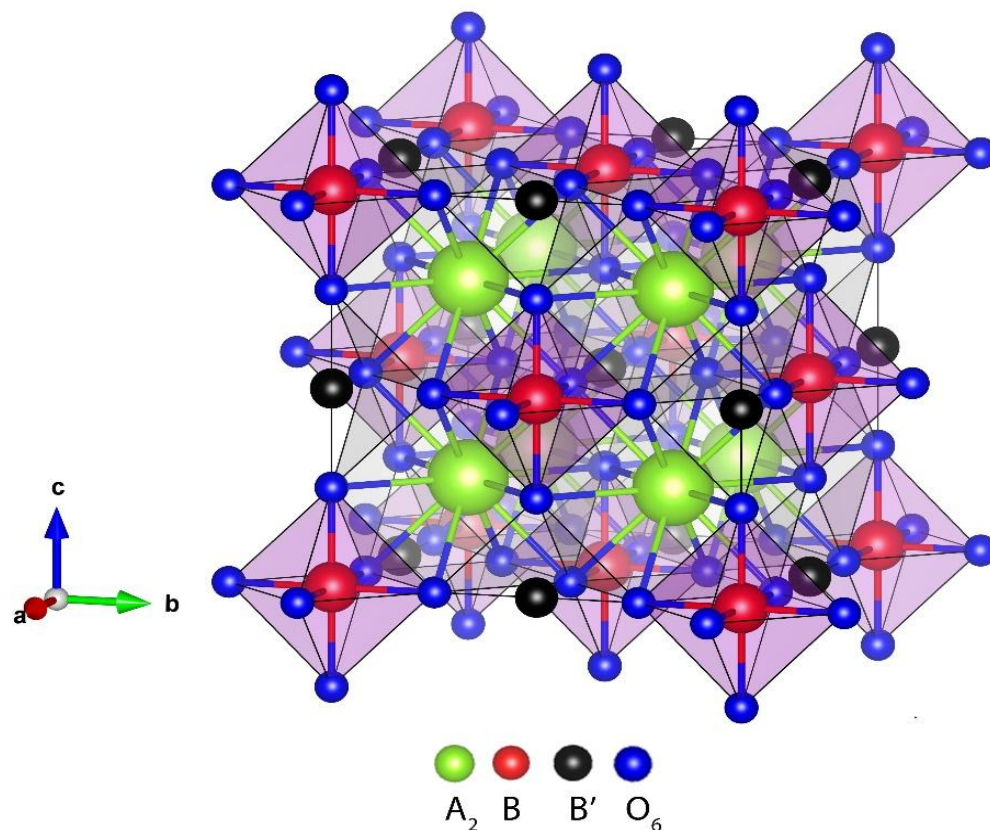


Fig. I.5: Schematic representation of the double perovskite crystal structure $A_2BB'_2O_6$.

1.4.2. Structural characteristics of $AA'BB'O_6$ double perovskite

Unlike traditional structures, $AA'BB'O_6$ denotes a double perovskite with ordered arrangements at both the A and B-site. This intricate structure hosts two distinct cations (A and A') at the A-site and two different cations (B and B') at the B-site, arranged in a regular, alternating pattern [77]. Such dual-site ordering is relatively rare and necessitates substantial disparities in size, charge, or bonding affinities among the cations. This configuration, compared to $AA'B_2O_6$ (**Fig. I.6**), often results in enhanced electronic and magnetic properties, making $AA'BB'O_6$ highly attractive for sophisticated functional applications. The $AA'BB'O_6$ structural type combines the layered ordering of A' without vacancies with the rock-salt ordering of B'.

This type of structure was not widely known until a little more than a decade ago, when structural stabilizing forces were first recognised, allowing for a targeted search for new members [78–82]. Some materials, like $BaLaB_2O_6$ or $NaLaB_2O_6$, are notable examples. These compounds are intriguing due to their potential to exhibit properties such as ferroelectricity or ionic

conductivity, which makes them valuable in advanced material science and applications. Large yet subtle structural modulations have been reported in $AA'B_2O_6$ perovskite, with octahedral tilt twinning playing at least a partial role in their formation [83].

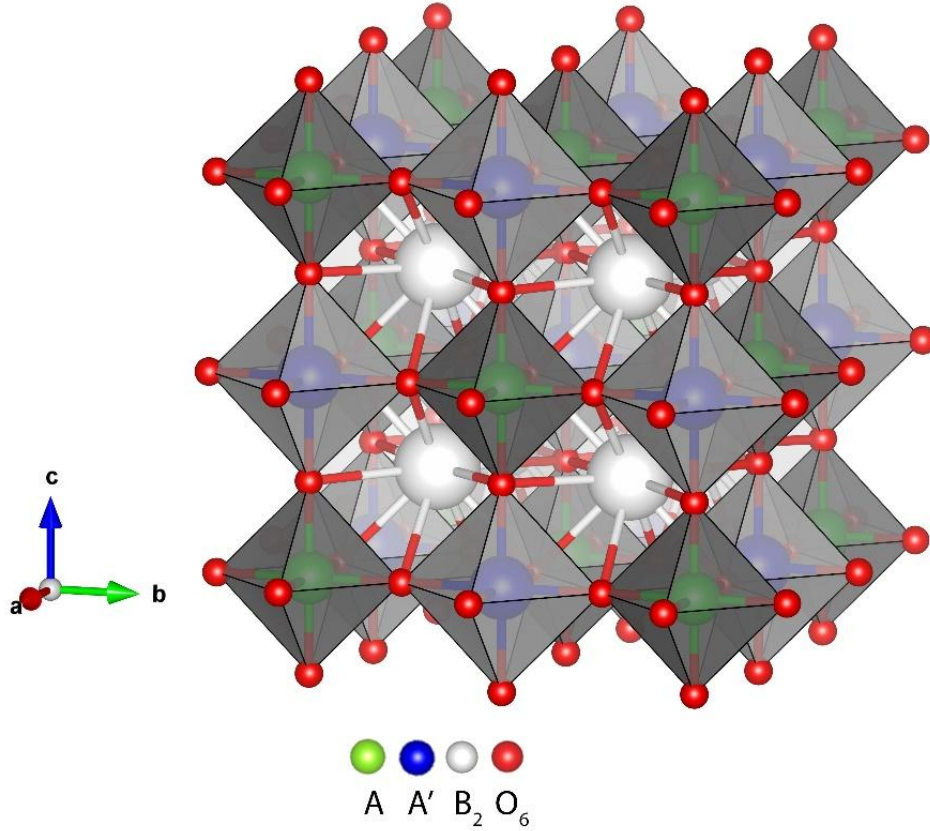


Fig. I.6: Schematic representation of the double perovskite crystal structure $AA'B_2O_6$.

The tolerance factor determines the structural stability of perovskites and double perovskites. The tolerance factor (t) for a double perovskite is given by Goldschmidt's formula.

$$t = \frac{r_A + r_{A'} + 2r_O}{\sqrt{2}(r_B + r_{B'} + 2r_O)} \quad (I.4)$$

And with doping (Tm^{3+}):

$$t = \frac{r_A + (1-x)r_{A'} + xr_{Tm} + 2r_O}{\sqrt{2}(r_B + r_{B'} + 2r_O)} \quad (I.5)$$

With r_A , $r_{A'}$, r_B , $r_{B'}$, and r_O representing the radii of elements A, A', B, B', and O, respectively.

1.5. Chalcogenides based-perovskite

Perovskite chalcogenides are a group of materials that integrate the perovskite crystal architecture with chalcogenide anions, such as sulfur (S), selenium (Se), or tellurium (Te), replacing the usual oxygen found in oxide perovskites. Chalcogenide perovskites constitute an essential class of non-oxide perovskite materials. These materials have primarily been investigated through computational studies, in which several groups have screened numerous chalcogenide perovskite compounds of the formula ABX_3 ($A = \text{Ca, Sr, or Ba}$; $B = \text{Ti, Zr, or Hf}$; $X = \text{S or Se}$) having band gaps between 0.30 and 2.30 eV [13,84]. The BaZrS_3 compound has received a lot of attention lately as a possible stable and lead-free photoabsorber [22]. Strong light absorption and great stability in ambient air are suggested by the thin-film synthesis studies [85–87]. The photovoltaic properties of these materials are predicted by a number of studies using computational analysis and DFT simulations [18,88,89].

1.5.1. Physical Properties of Perovskite

The distinct structure and atomic arrangement of perovskite chalcogenides are tightly linked to their physical properties, setting them apart from conventional oxide and halide-based perovskites. These substances often have the structures ABX_3 or $A_2BB'X_6$, where X represents a chalcogen element such as tellurium (Te), selenium (Se), or sulfur (S). These materials flexible crystal lattices increase the range of applications by permitting structural deformations and the formation of low-dimensional structures. Whereas weaker bonding relative to oxides may decrease thermal conductivity (beneficial for thermoelectric applications), the inclusion of heavier chalcogen atoms typically results in greater material density.

1.5.2. Electrical, stability, and optical properties

1.5.2.1. Electrical properties

Perovskites are a class of crystalline materials with the general formula ABX_3 , and possess exceptional electrical properties, enabling them to be used in various applications. They are known for their outstanding dielectric, photovoltaic, and piezoelectric properties, which derive from their unique crystal structure and the flexibility of the A and B sites, which can accommodate a variety of elements. In their native form, perovskites generally exhibit high ionic conductivity, making them ideal solid electrolytes for batteries and fuel cells. In addition, some perovskites are

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characterised by their ability to adjust energy gaps and strongly absorb light, which is essential for photovoltaic applications, particularly in perovskite solar cells. Due to their high thermal stability, this class of materials offers opportunities for alternative thermoelectric materials with a plentiful and earth-friendly composition [21].

The energy bands that are available to electrons in crystals are represented in reciprocal space as a function of the wave vector k along the symmetry directions in the first Brillouin zone (refer to [Fig. I.7](#)). The smallest volume that completely encompasses the perpendicular bisectors of the reciprocal lattice vectors, beginning at the origin, is known as the Brillouin zone. The material's electronic properties are primarily determined by the band gap between the valence-band maximum and the conduction-band minimum.

Since the Brillouin zone represents the symmetry of the crystal lattice in wave space, it varies depending on the crystal structure of the material. The first Brillouin zone has a cubic shape in a simple cubic lattice. The face-centred cubic (FCC) lattice is represented by a truncated octahedron. In a body-centred cubic (BCC) lattice, it appears as a rhombic dodecahedron. These variations in shape provide evidence of the diverse crystal symmetry and a variety of crystallographic orientations.

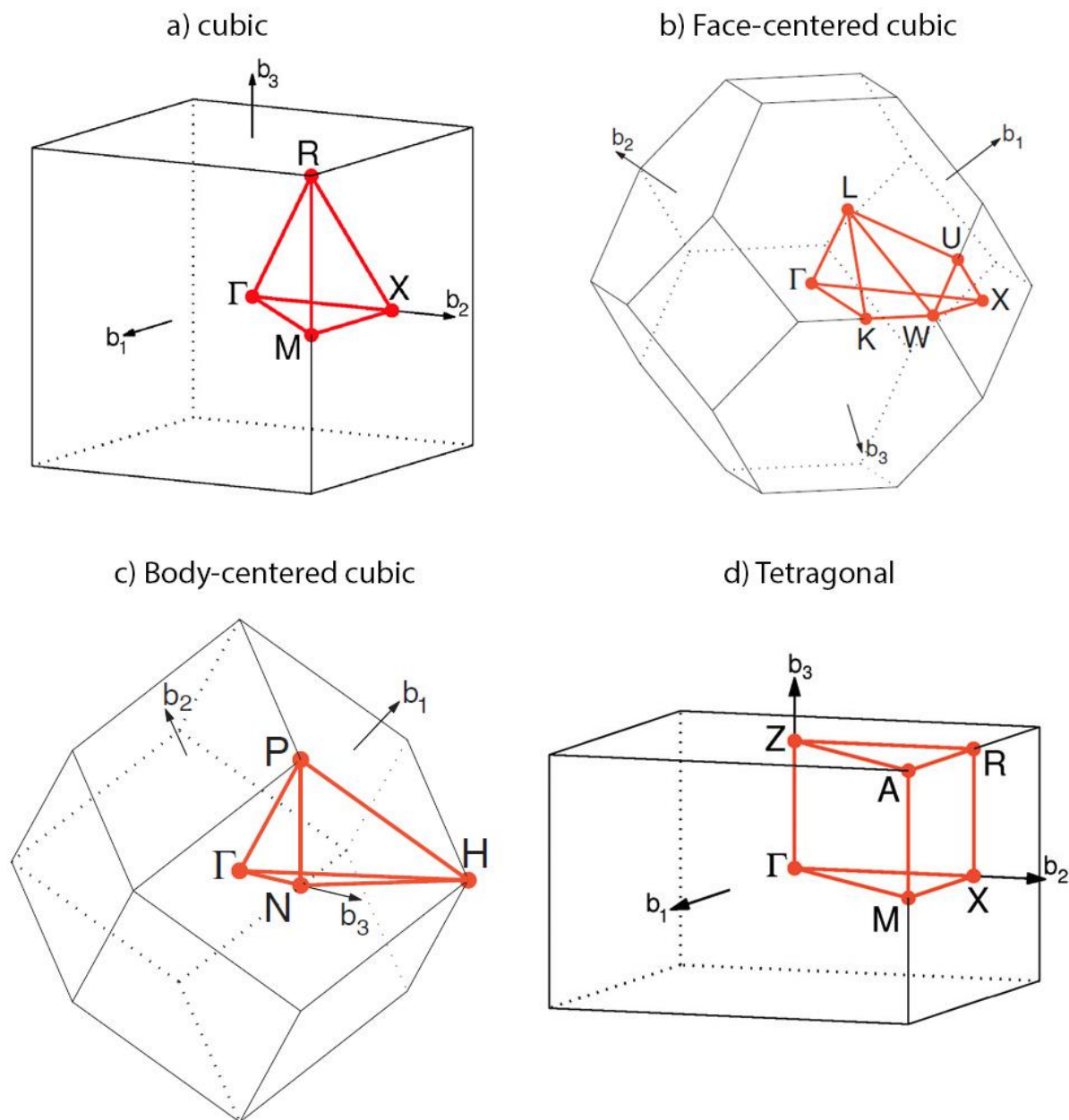


Fig. 1.7: The first Brillouin zone: cubic structure (a), face-centered cubic structure (b), body-centered cubic (c), and tetragonal (d) [90].

The predicted band gaps for the three phases of each of the 18_ABX₃ compounds are shown in **Fig. 1.8**, based on these band gaps and absorption properties, the authors identified intriguing solar-cell materials in the deformed perovskite phases of BaZrS₃, CaHfSe₃, CaZrSe₃, and CaTiS₃ [13]. Computational studies were the primary method used to study this kind of material, predicting diverse interesting properties and desirable optical band gaps that are suited for

optoelectronic applications, with energy gaps ranging from 1 to 2.8 eV. Reports suggest that experimental synthesis of materials with predicted direct band gaps of about 1 eV may be useful for solar applications [13,14]. SrSnSe_3 , CaSnS_3 , and SrSnS_3 are among the estimated chalcogenide perovskites with adjustable direct band gaps in the ideal range of 0.89–1.59 eV for single-junction solar cell applications [91].

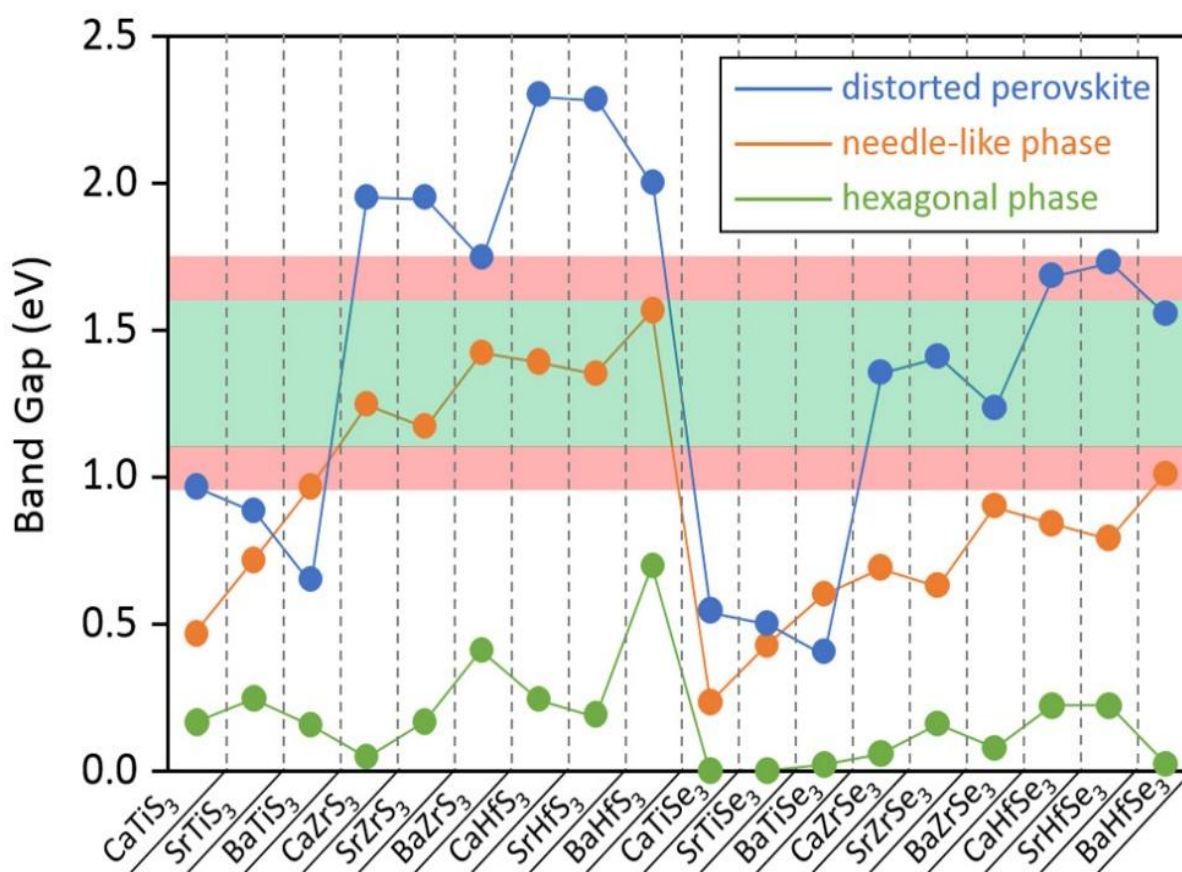


Fig. I.8: Calculated band gaps of eighteen ABX_3 compounds using the HSE_{06} functional. reproduced with permission from [13]. (2015) by the American Chemical Society.

Fig. I.9 shows the abundance of specific elements essential for photovoltaic cells in the Earth's crust, focusing on the yellow elements present in chalcogenide perovskites. Except Hf and Se, all the elements listed are among the 20 most abundant and appear in greater abundance than components such as Zn, Cu, Pb, etc [92].

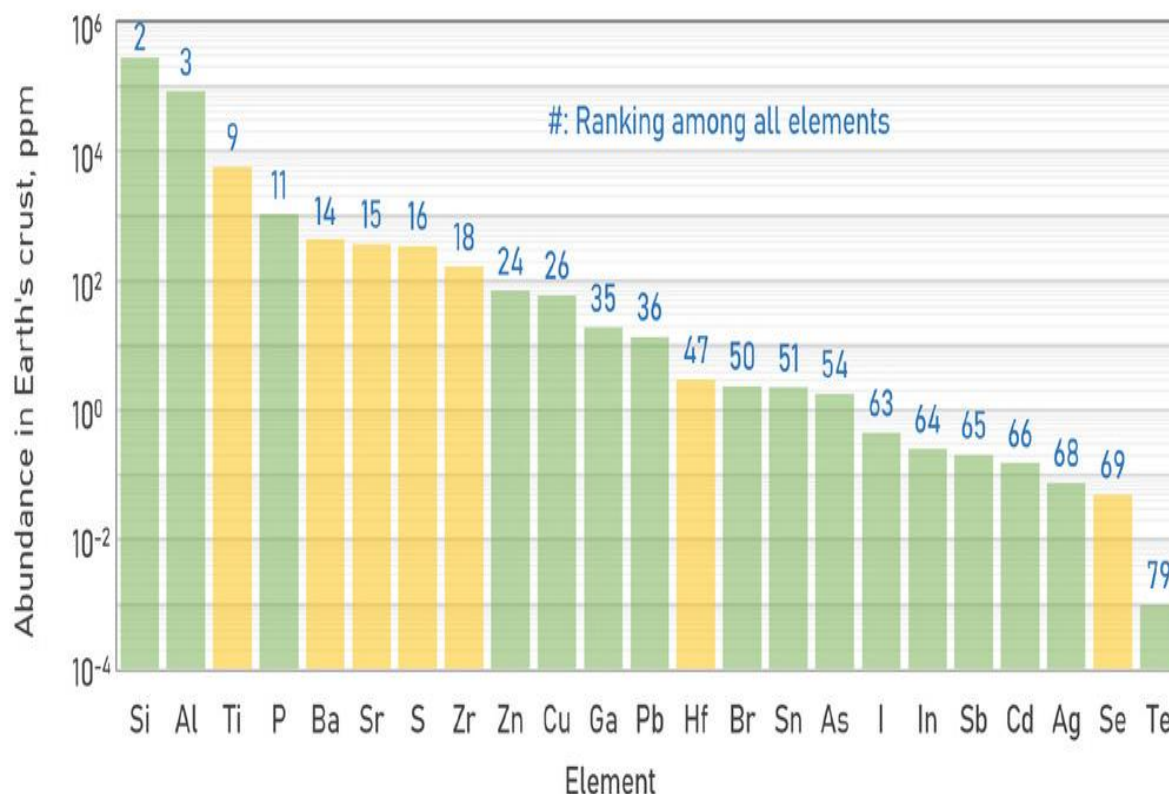


Fig. I.9: The yellow highlights represent the components of chalcogenide perovskite, and the study indicates the abundance of the basic components used in photovoltaic technologies.

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I.5.2.2. Stability and optical properties

The stability of a crystal lattice can be evaluated by comparing the lattice energies of different structures that share the same chemical composition. This approach helps to identify the most energetically favorable arrangement. When we talk about perovskites, it is worth mentioning hybrid lead halide perovskites (organic and inorganic), considered among the throne of the third generation of energy absorbers, as they have appeared in research papers with high absorption results and impressive physical properties. This generation's photovoltaic efficiency has improved significantly, reaching 26.9% in 2025-2026 [94–96].

Despite its high performance, mechanical stability was the main obstacle, along with toxicity due to the presence of lead and degradation damage when used in industrial applications. This led to the hypothesis of searching for new perovskite-based inorganic materials that would be free of

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these drawbacks and have greater longevity. Chalcogenide perovskites are one of the materials that have been recently studied and have attracted several groups [13,97–99]. Compared to lead (Pb), chalcogenide perovskites are composed of elements with a lower environmental impact [87]. High absorption coefficients can be achieved with chalcogenide perovskites, thereby increasing their efficiency as photoabsorbers [100]. The enhancement in their electronic and optical properties can be attributed to their covalent nature, which facilitates superior charge transport and curtails recombination losses [99]. Chalcogenides-based materials have a high absorption coefficient exceeding 10^4 cm^{-1} , a favourable direct bandgap that can be adjusted between 0.99 and 1.99 eV, good thermal stability, and minimal toxicity [101]. Therefore, they are promising materials for use as absorbers.

I.6. Conclusion

In this chapter, we presented a thorough overview of the structural variability and stability of perovskite materials, particularly those with the general formula ABX_3 , along with their extended double perovskite variants. We examined a range of crystallographic phases, including monoclinic, triclinic, orthorhombic, tetragonal, and rhombohedral forms, which effect the physical and electronic properties of perovskites. Important stability factors, such as the tolerance factor and the characteristics of anion-cation bonding, were analysed to understand the formation and durability of these structures. Additionally, we explored the complex arrangements found in double perovskites such as $\text{A}_2\text{BB}'\text{X}_6$ and $\text{AA}'\text{BB}'\text{O}_6$, which enhance functionality and tunability. The discussion of chalcogenide-based perovskites highlighted their promising physical, electrical, and optical properties, underscoring their potential for next-generation optoelectronic applications. This foundational knowledge lays the groundwork for deeper investigations into perovskite-based materials and their practical applications.



Chapter II: Overview on PV solar cells: materials and technologies.

II.1. Introduction to photovoltaic (PV) solar cells

The solar cell is a device that uses photoelectric effect to capture and directly convert the energy of sunlight rays into electricity. The discovery of the first photoelectric effect by *Becquerel* (1839) was a significant moment in the development of solar cells, and he demonstrated that the cell generates more power when exposed to sunlight [102]. All photovoltaic devices operate based on a PN junction within a semiconductor that produces current and voltage [103].

A solar cell usually consists of an absorber layer that effectively captures photons from incident radiation to generate electron-hole pairs. To maintain the separation of these photo-generated electrons and holes, semi-permeable membranes are attached to both sides of the absorber. Additionally, the cell must convert the absorbed energy into free electrical charges and transfer them through an external electrical circuit (see *Fig. II.2*).

The evolution of this technology has shown significant progress, particularly in its use in space and terrestrial applications. Efforts are underway to reduce production costs and improve efficiency for a wider range of applications. PV systems are distinguished by the materials and technology used in their solar cells. Generally, there are four generations of PV cell technology as illustrated in *Fig. II.1*.

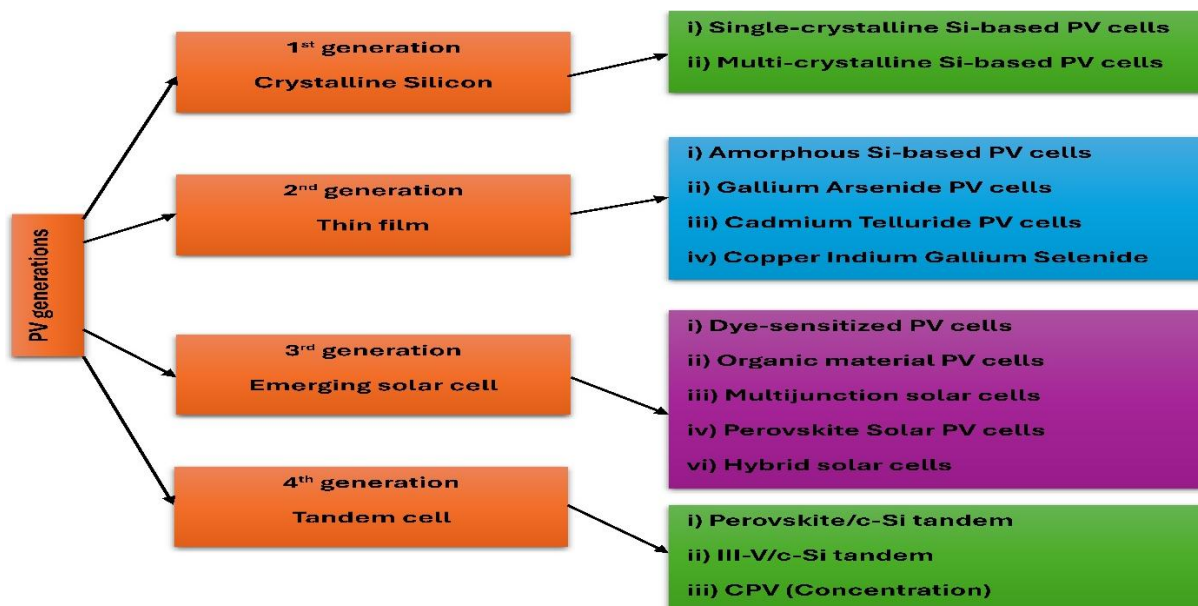


Fig. II.1: Classification of photovoltaic (PV) cell types [104].

II.2. First-Generation photovoltaics: the age of silicon technology

The silicon solar cell, considered the first generation of photovoltaic (PV) technology, was developed in 1954 and is made up of two types of silicon: p-type and n-type [105], as shown in **Fig. II.2** [106]. At present, it holds a market share of more than 90% [107]. Silicon, which makes up about 28% of the earth's crust, is abundant and crystallizes to form bulk material for various applications [104].

The P-type silicon is created by doping the silicon with boron atoms, which leave "holes" where electrons are absent. In contrast, n-type silicon is formed by doping with phosphorus atoms, which introduce additional free electrons. When the p-type and n-type silicon are joined together, the electrons from the n-type region move to fill the holes in the p-type region at the junction, resulting in the formation of a depletion region. This depletion region produces an internal electric field that enables the solar cell to generate electricity when it is exposed to sunlight. Recent advancements in photovoltaic technology focus on increasing energy output while reducing manufacturing costs and time, enhancing cell efficiency, and lowering module production expenses.

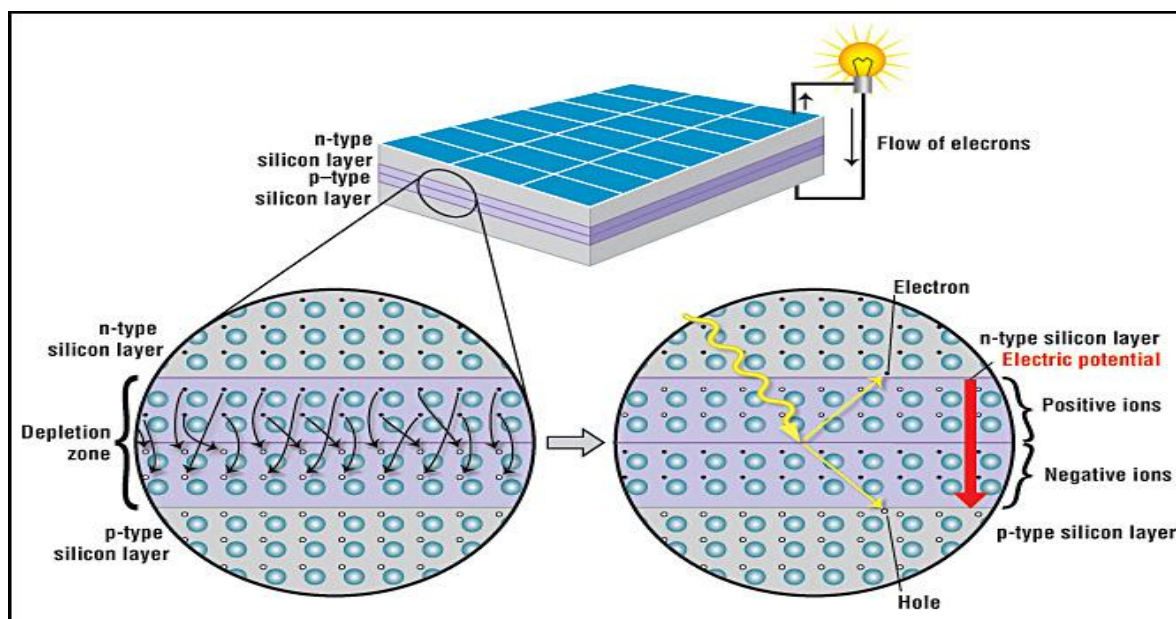


Fig. II.2: The diagram of a solar cell shows the n-type and p-type layers, as well as the depletion zone at the junction [106].

II.2.1. Monocrystalline silicon cells

These cells have a continuous crystal lattice structure with minimal defects or impurities and are composed of pure silicon. The Czochralski (CZ) process is used to draw a cylindrical ingot from a single crystal to create monocrystalline silicon. This specific type of solar cell can be seen in *Fig. II.3*.

One important advantage of monocrystalline cells is their remarkable efficiency. Their bandgap ranges from 1.11 to 1.15 eV. The most common photovoltaic (PV) technology available today, single-crystalline silicon (Sc-Si) solar cells, exhibit exceptional performance, achieving efficiencies of 20-24% in commercial applications and 27.8% in laboratory testing [108–111].

However, a significant disadvantage is that monocrystalline silicon production requires a complex and labour-intensive manufacturing process, thereby increasing production costs relative to alternative technologies.



Fig. II.3: View from both sides of monocrystalline solar cells [112].

II.2.2. Poly-crystalline silicon cells

During the production process, molten polycrystalline silicon is cast into ingots, then thinly sliced into wafers, and finally assembled into full solar cells [108]. Polycrystalline silicon cells are created by combining several silicon crystals that cool slowly over several hours. Polycrystalline silicon (Mc-Si) solar cells often achieve laboratory efficiency of 24.4% [109–111]. One significant disadvantage is that, although Mc-Si cells are generally less expensive to produce, they still have a more complex and costly production process than monocrystalline (Sc-Si) cells. A typical polycrystalline solar cell is depicted in *Fig. II.4*.

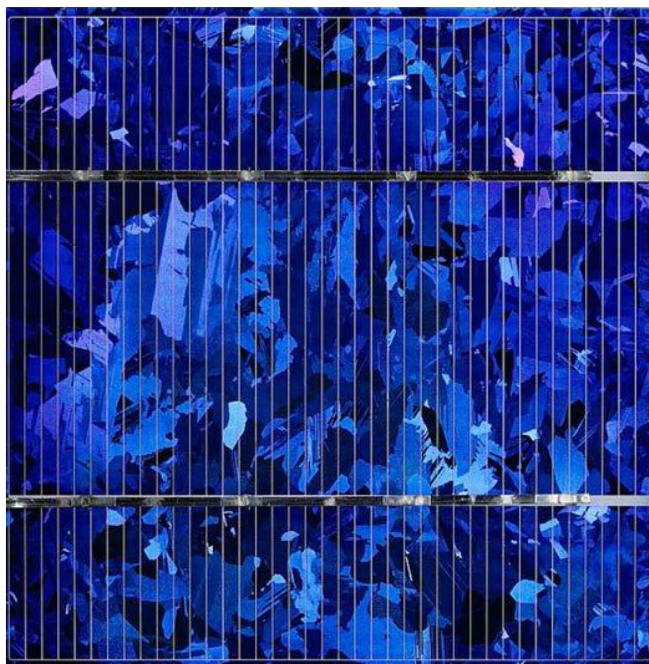


Fig. II.4: Poly-crystalline silicon solar cell [112].

II.3. Second-generation of PV cells

The term thin-film solar cells refer to second-generation solar cells because they are composed of layers that are only a few micrometres thick compared to crystalline silicon-based cells. Compared to first-generation solar cells, second-generation solar cells perform better by around 15% to 20% [113]. Compared to a conventional first-generation c-Si solar cell, thin films can range from 200 nm to tens of micrometres making them noticeably thinner [114]. After extensive basic and applied research by multiple scientists and engineers worldwide, a substantial solar energy

sector utilising thin films of amorphous silicon-hydrogen has developed in various countries. Despite years of rigorous development and production, it has not succeeded in challenging the supremacy of crystalline silicon, primarily due to the higher cost, reduced efficiency, and relative instability compared to crystalline silicon cells. Despite silicon's dominance, thin film technologies have long been known for their advantages. Their heat tolerance has been enhanced, they are more suitable for low-light conditions, they can be deposited on a variety of substrates, and the thinness of their absorption layers enables the production of transparent or semi-transparent modules.

II.3.1. Amorphous silicon

The first amorphous silicon (a-Si) solar cells were introduced in 1976. This type of silicon is commonly used in devices that require minimal power, such as parking meters, lighting, and calculators. Nonetheless, some manufacturers offer modules that are comparable in size to crystalline silicon modules. The production of thin films of amorphous silicon is achieved through CVD plasma-enhanced chemical vapour deposition (PECVD) [115].

It is possible to deposit the layers into both rigid substrates, such as glass, and flexible substrates, such as thin metallic sheets and plastics, enabling continuous production and a variety of uses. About 5% hydrogen atoms, which aid in the reduction of weak bonds, are present in hydrogenated amorphous silicon (α -Si: H), the material used to make solar cells and absorb higher energy photons; this type has an optical absorption coefficient larger than 10^5 cm^{-1} and a direct optical energy band gap of 1.7 eV [116]. The thickness of silicon used to make solar cells has been reduced to a few microns by amorphous silicon, which has a superior optical absorption coefficient than monocrystalline silicon. This significantly reduces the risks and costs associated with raw materials, given the scarcity caused by the silicon shortage [117,118].

II.3.2. Cadmium telluride (CdTe) solar cells

One popular technique for combining cells into modules in thin film photovoltaic (PV) technology is monolithic integration. This technique involves applying thin, electrically active coatings onto inexpensive substrates (such as glass), followed by scribing and back-contact processes to produce interconnected cells [119].

Second-generation solar cells have serious disadvantages despite being less costly. Risky materials are used in the production and disposal of many devices, such as Cadmium Telluride

Chapter II: Overview on PV Solar cells: materials and technologies.

(CdTe). The thin-film layers of cadmium telluride (CdTe) used in solar cells function as semiconductors, converting absorbed sunlight into electricity. Two electrodes are used in these solar cells: one is made of copper-doped carbon paste, and the other is made of tin oxide or stannous oxide doped with cadmium [120]. In 1982, Kodak created the first CdTe-based cell with an efficiency greater than 10% and an absorption band gap of 1.4eV [112]. Cadmium telluride (CdTe) thin-film photovoltaic (PV) modules are the most widely available thin-film product on the international market, with a peak (GWp) production capacity of approximately 32 GW. From a production line producing 25 MWp annually in 2005 to a target of 21 GWp annually by 2024, the U.S.-based company has expanded the use of these modules to millions of sites globally, primarily in utility-scale power plants [119]. This impressive advancement is a result of both the technology intrinsic economics and the more than doubling of module power conversion efficiency (PCE) from around 9% to slightly over 19% during this time [121]. By breaking through the \$1/Wp barrier, CdTe technology spurred enormous investment in PV manufacturing, lowering the cost of PV electricity generation below that of several fossil fuels [122]. By 2015, the efficiency of research-scale record cells had increased from 16.5% in 2001 to over 22% [123,124]. The schematic cell material stacks for CdTe-based cells that are used currently, previously, and prospectively are shown in *Fig. II.5* [119].

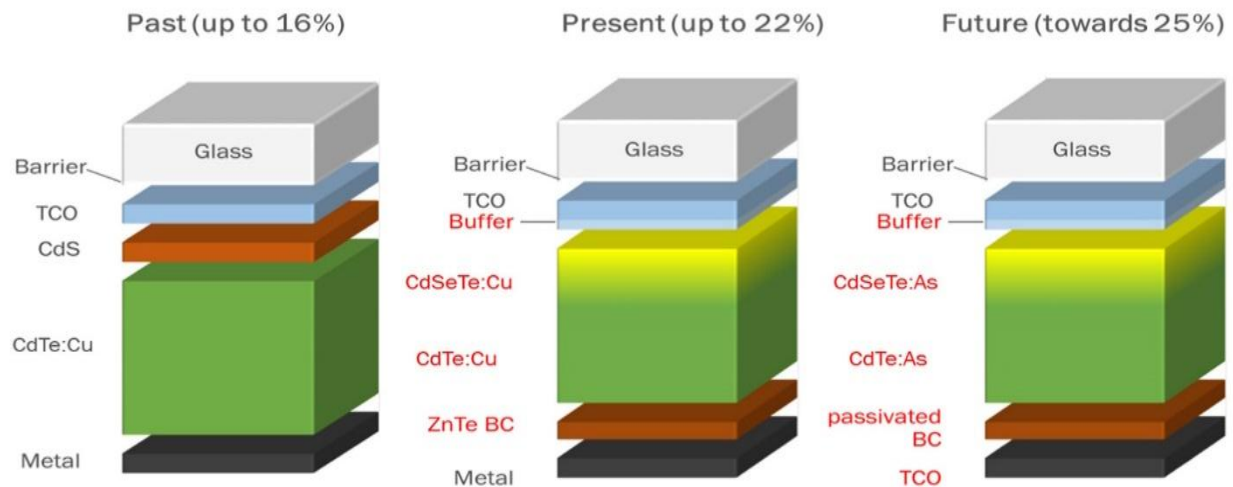


Fig. II.5: A comparative overview of efficiency trends in CdTe-based solar cell developments and configurations [119].

II.3.3. Copper indium gallium selenide solar cells (CIGS)

In the PV sector, silicon-based technologies and thin-film alternatives have long been at odds, and this competition has persisted during the most recent phase of rapid expansion. Thin-film solar cells are enabled by copper indium gallium selenide (CIGS), making it an intriguing material in the field of solar energy. With a thin layer that uses fewer resources, these cells are highly effective at converting sunlight into electrical energy. Its strong absorptivity further enhances its capacity to absorb sunlight effectively. Mono- and multi-crystalline Si systems have consistently outperformed thin-film systems in terms of production volume; they made up 94% of the world's production (77.7 of 82.6 GWp), with the remaining percentage including amorphous-Si (α -Si) PV, cadmium-telluride (CdTe), and copper indium gallium-selenide (CIGS) [125]. With a record of 19.2% compared to 19.9% and 24.4% for multi- and mono-crystalline Si, respectively, 18.6% for CdTe, and 11% for α -Si, CIGS is now the closest competitor to Si systems at the laboratory scale [125].

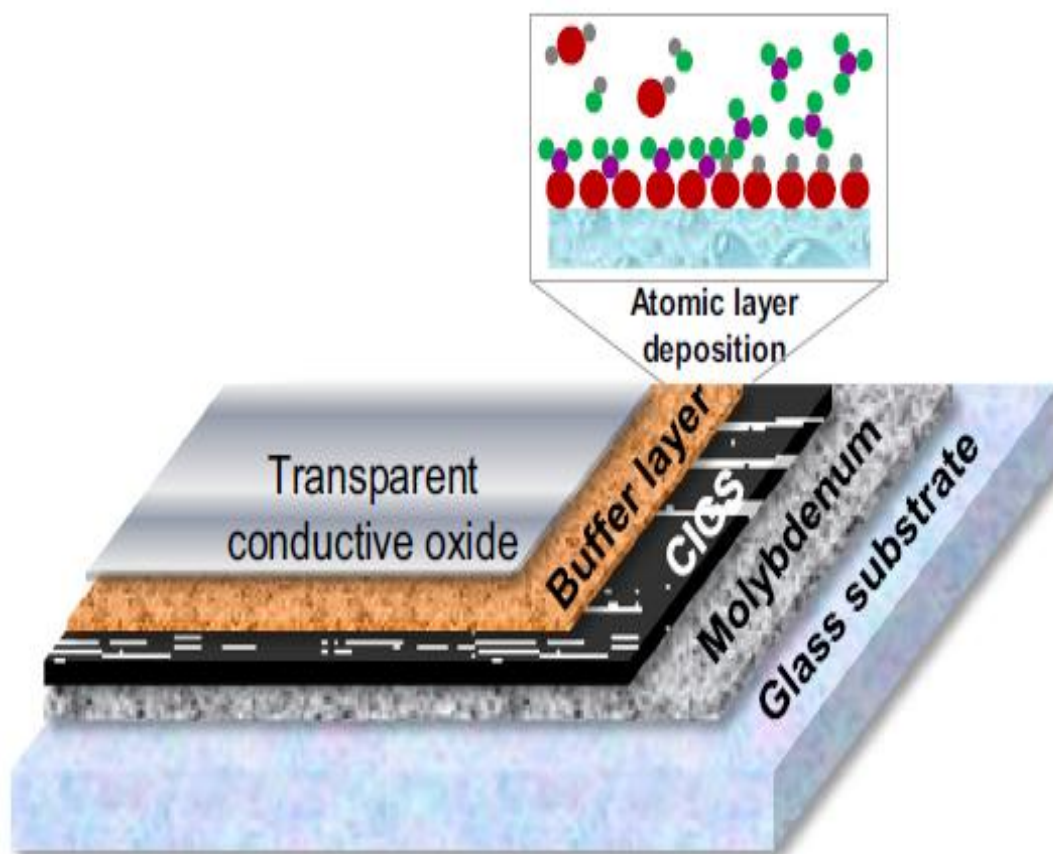


Fig. II.6: Designed solar cells of CIGS module [126].

II.4.Third-generation: emerging solar cell

Green [127] defines third-generation solar cells as those that combine high power-conversion efficiency with lower production costs. These cells aim to significantly improve efficiency while maintaining the cost and environmental benefits of thin-film deposition. Third-generation PV technologies target costs well below the \$1/W level of second-generation PVs, aiming for \$0.50/W or even \$0.20/W (see [Fig. II.7](#) for the three PV generations) [128].

Third-generation PV technologies, such as dye-sensitized, organic, and perovskite cells, remain at the forefront of laboratory innovation. For years, dye sensitisation struggled to gain traction, but in 1991, Grätzel and his team at the Laboratory of Photonics and Interfaces in Switzerland sparked a breakthrough by merging nanostructured electrodes with efficient charge-injection dyes to create a new kind of solar cell [129].

A dye-sensitized solar cell (DSSC) is a sophisticated system designed for light-to-electricity conversion. Its basic structure closely resembles the original Grätzel cell design. [Fig. II.8](#) presents a schematic of the DSSC structure [130].

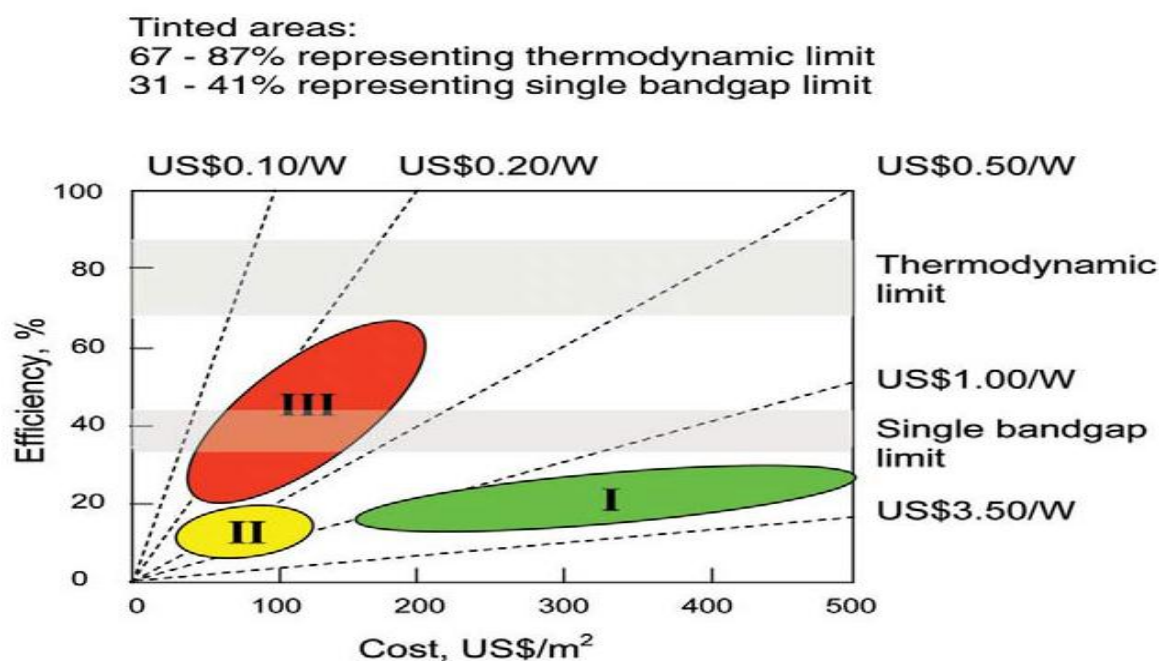


Fig. II.7: Projected efficiency and cost for first- (I), second- (II), and third-generation (III) photovoltaic (PV) technologies, corresponding to wafer-based, thin film, and advanced thin film systems, respectively (2007) [128].

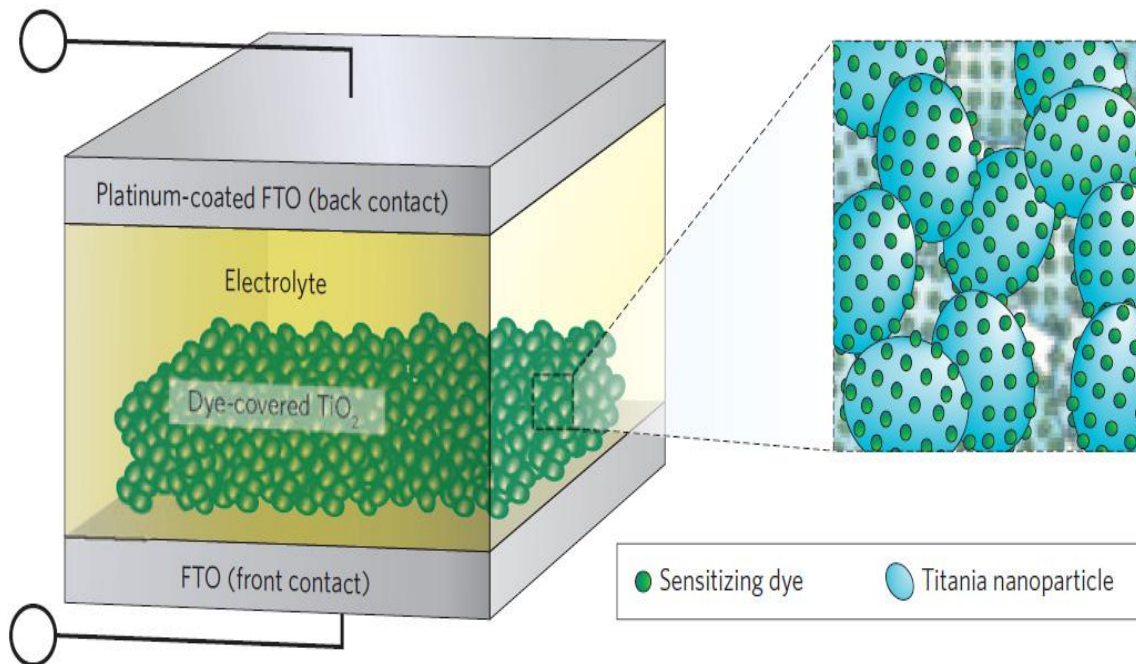


Fig. II.8: Visual overview of how a dye-sensitized solar cell is structured and operates [130].

Multijunction solar cells use multiple layers of different semiconductor materials. Each layer absorbs radiation not captured by the previous one, allowing the device to convert more incident light into electricity. This design results in higher efficiency compared to single-junction cells. As depicted in [Fig. II.9](#), the energy conversion mechanism of the III-V triple junction solar cell where each subcell absorbs a distinct portion of the solar spectrum based on its bandgap. The spectral irradiance for AM1.5, the standard terrestrial solar spectrum, is given in power density units ($\text{W}/\text{m}^2/\text{nm}$), along with the fractions each subcell can convert based on the detailed balance efficiency limit [131]. High-energy photons are absorbed by the top cell (usually made of GaInP), the intermediate part of the solar spectrum is absorbed by the middle cell (usually made of GaInAs), and the low-energy photons transmitted through the cells above are converted by the bottom cell (usually made of germanium) [132].

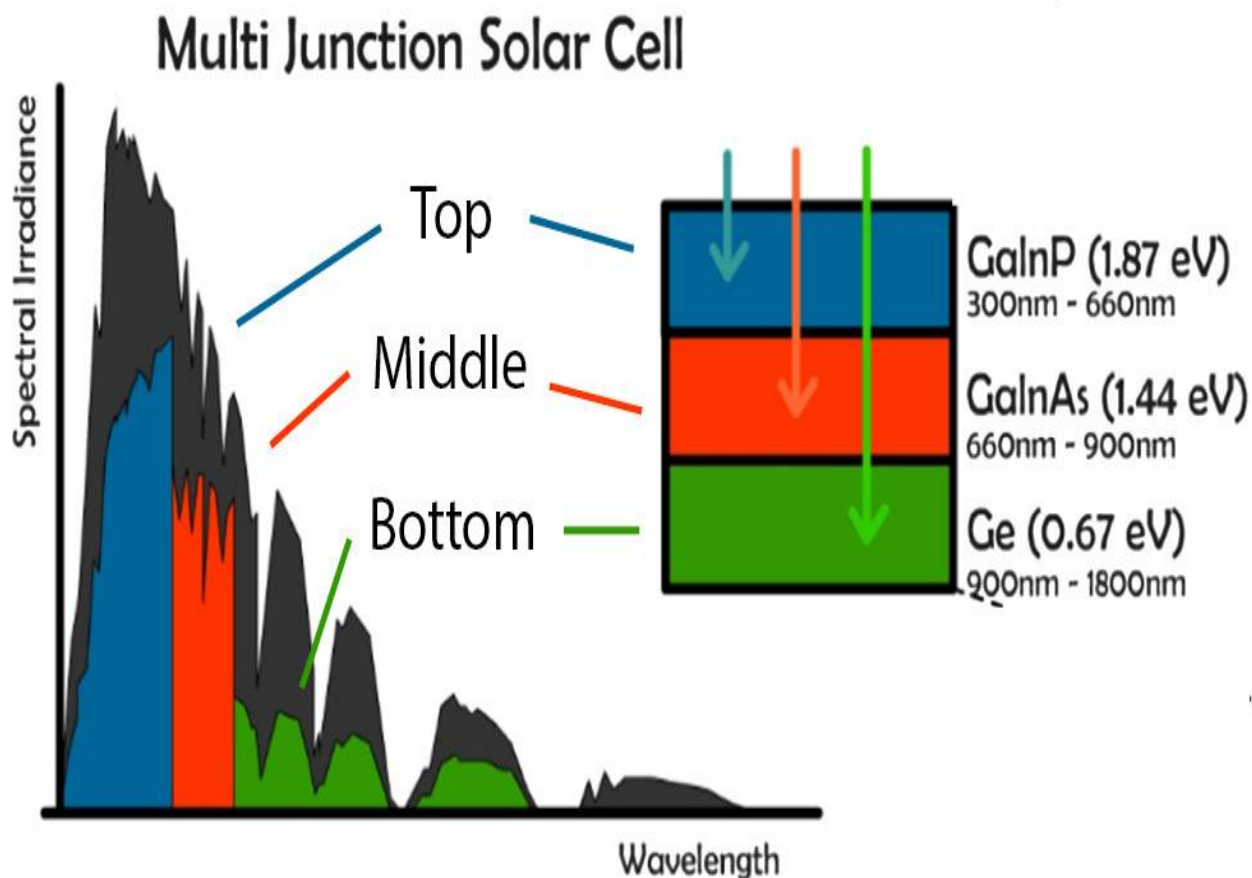


Fig. II.9: AM1.5D solar spectrum and theoretical spectral utilization by a multijunction GaInP/GaInAs/Ge solar cell [131].

II.5. Fourth-generation photovoltaics: tandem solar cells

Most PV cells on the market have an efficiency of 20–25% [104]. The efficiency of single-junction c-Si is nearing its theoretical limit of 29.4% [133]. Perovskite tandem solar cells represent a prominent class of photovoltaic devices characterized by their high-power conversion efficiency. These devices typically integrate a wide-bandgap perovskite cell with a bandgap of approximately 1.7 to 1.8 eV, and a silicon (Si), copper indium gallium selenide (CIGS), or organic cell, each with a narrower bandgap near 1.1 eV [134].

Fourth-generation solar cells, the latest advancement in this field, are the result of efforts to improve solar cell stability and efficiency. They offer the combined advantages of previous generations, including lower cost, flexible structures, and the high stability provided by

nanomaterials [135]. These devices are known as hybrid solar cells because they integrate inorganic materials—such as metal oxides and metal nanoparticles—with organic components like carbon nanotubes, graphene, and their derivatives [136,137]. **Fig. II.9** presents the efficiencies of different generations of solar cells alongside their respective development timelines.

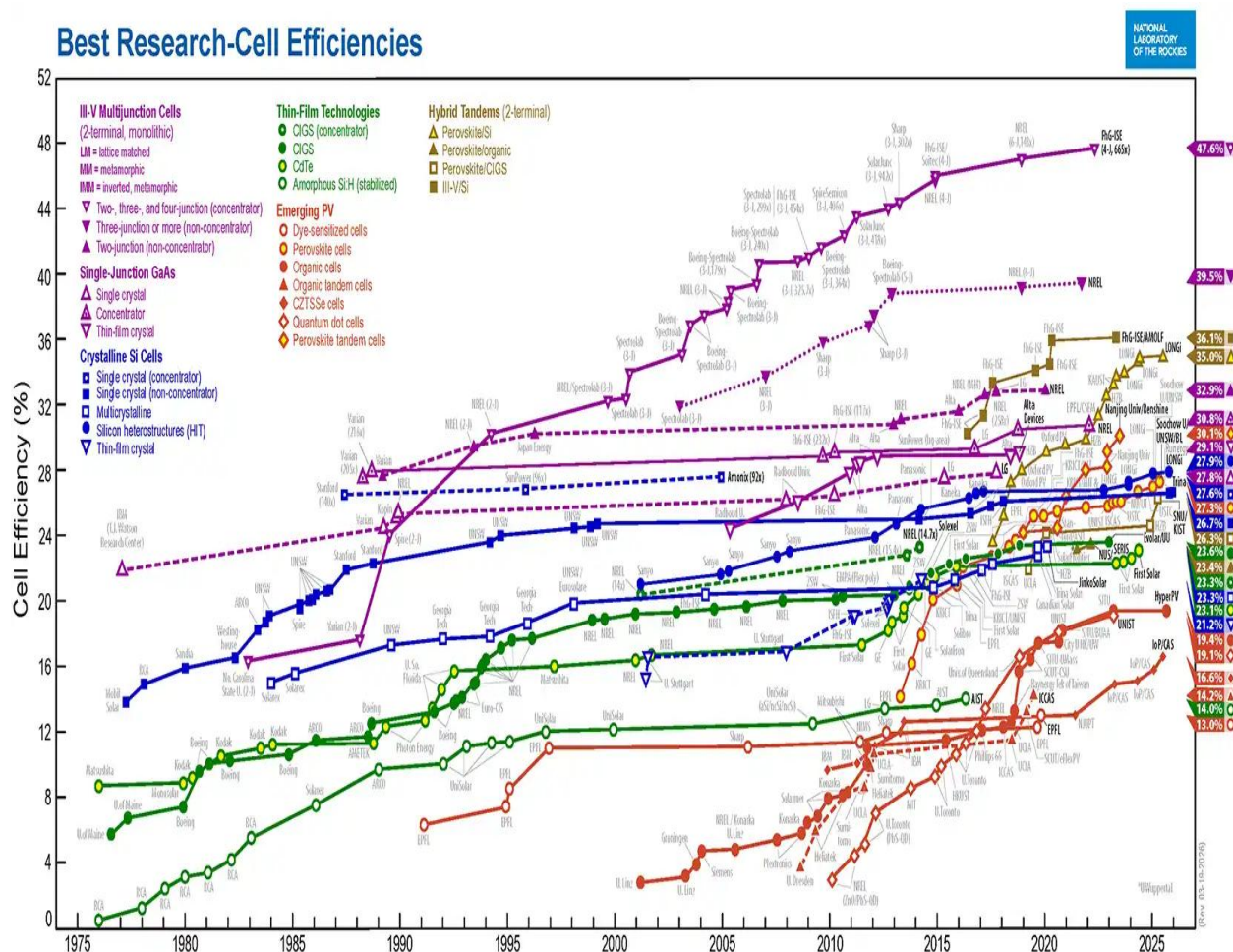
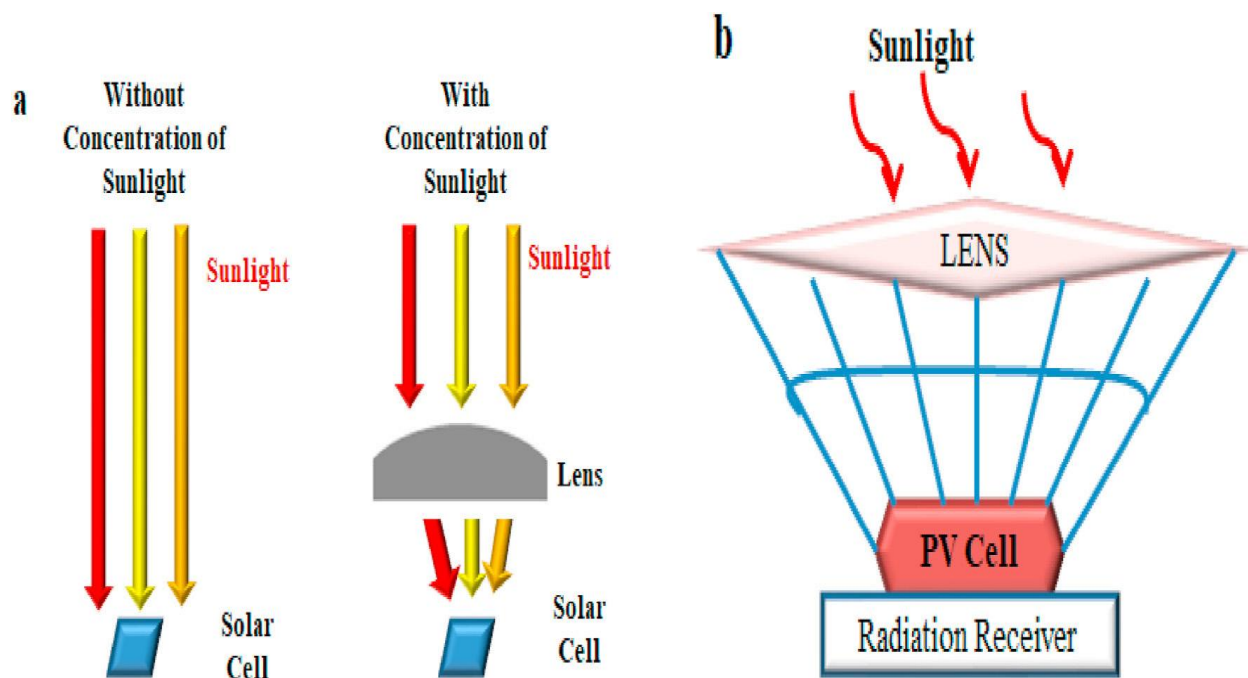


Fig. II.9: Progress in solar cell efficiency (2025) [138].

The CPV cell was developed in the 1970s [139]. Concentrated photovoltaic is a technique that generates significant power using smaller solar cell areas; since the solar modules absorb more solar radiation, less PV rooftop coverage is needed. By assembling large concave mirrors and convex lenses, this method uses ray optics to focus sunlight onto a small area of the solar cell, generating a significant amount of thermal energy [132,140]. The fundamental structure of this process is depicted in **Fig. II.10 a)**, and its schematic representation is shown in **Fig. II.10 b)** [141]. This innovation has produced promising results.



a Basic layout; and **b** Schematic structure of Concentrated photovoltaic cell

Fig. II.10: schematic representation of sunlight concentration in concentrated photovoltaic (CPV) system [142].

II.6. Overview of perovskite solar cell structure

Perovskite materials have had a significant impact on manufacturing in terms of reducing production costs and improving performance. Solar cells have gone through three generations. The first generation consisted of traditional silicon cells, which were very efficient but also very expensive. Following this, the second generation of thin-film cells emerged, offering a lower cost alternative at the expense of decreased efficiency. These issues persisted until the arrival of the third generation, which features perovskite cells. These cells address many of the problems previously encountered. It must be mentioned that the standard perovskite solar cell (PSC) consists of a series of well-defined layers that include an n-type layer, a mesoporous oxide layer, a light-absorbing perovskite layer, a hole transport layer, and the two electrodes. The overall structure of a PSC is illustrated in **Fig. II.11**; it consists of several essential components [143]:

- ✚ **Substrate:** It is usually made of glass or flexible materials that support the cell's structure.
- ✚ **FTO/ITO Coated Glass:** Either FTO or ITO serves as the transparent conductive layer, allowing light to pass and through while providing electrical conductivity.
- ✚ **Hole Blocking layer:** Ensures efficient charge collection by preventing electrons from recombining with holes.
- ✚ **Electron Transport Layer (ETL):** Generally, it is made of ZnO or TiO₂ to facilitate electron transport between the perovskite layer and the electrode.
- ✚ **Perovskite layer:** Plays a crucial role in absorbing sunlight and generating electron-hole pairs.
- ✚ **Hole Transport Layer (HTL):** The main function of the HTL is to transport holes from the perovskite layer to the anode, which is typically made from materials such as spiro-OMeTAD or CuSCN.
- ✚ **Electrodes:** The anode is made from ITO or gold, and the cathode is made from silver or aluminium; their role is to collect, transport, and deliver the generated charges to the external circuit.

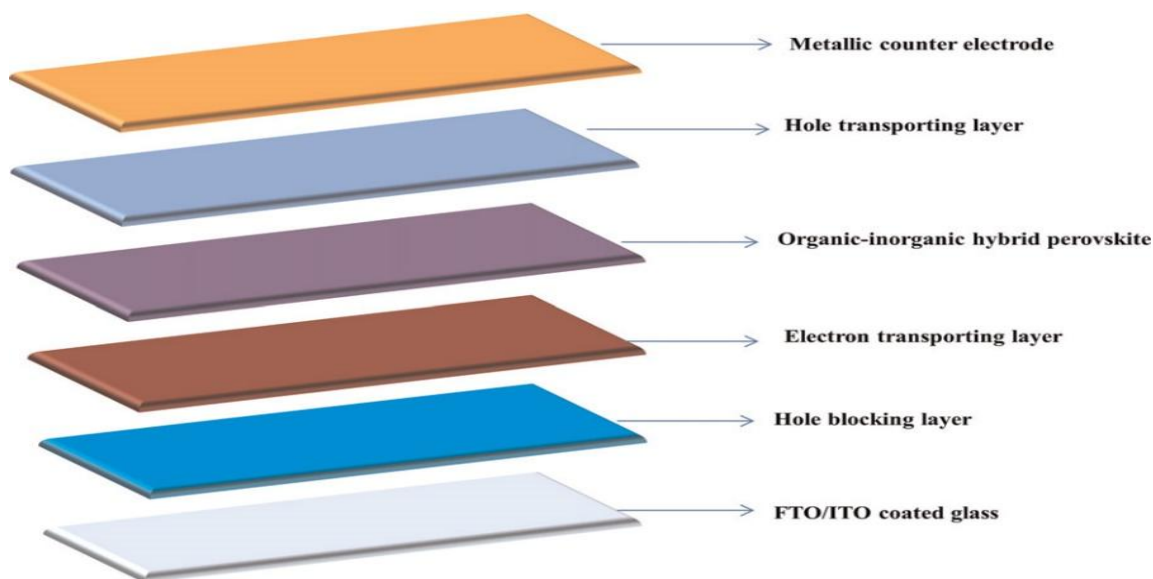


Fig. II.11: Schematic representation of the perovskite solar cell [143].

Perovskite solar cells (PSCs) have become popular in the thin-film photovoltaics industry due to their high-power conversion efficiency and low cost [144]. More recently, perovskite

chalcogenide cells have also appeared. Substituting oxygen with either sulfur or selenium is found to reduce the bandgap, making it useful for solar cell applications [16].

II.6.1. Mechanisms in perovskite solar cells

The process first begins with absorption by the perovskite layer in order to generate excitons, which are pairs of holes and electrons. It should be noted that perovskite materials do not have the same binding energy for the exciton and differ from compound to compound. These excitons allow the formation of free carriers, i.e., free electrons and holes, which allows electricity to be generated and recombined into excitons, with a low recombination probability in perovskite materials such as the $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) [145–147] as used in meso-superstructure solar cells (MSSCs).

In this process, perovskite materials play a key role. The method by which electrons pair with holes is known as the recombination process. The charge carriers required for current flow are absent when electrons are depleted. The hole transport layer (HTL) with FTO collects the holes, while electron transport layer (ETL) with TiO_2 captures the electrons. This layer receives electrons from the perovskite, and the metal electrode gathers the holes to produce photocurrent.

II.6.2. Unveiling the versatility of PSC designs

Many multi-junction photovoltaic designs, such as mesoporous stacked structures (MSSCs), planar heterojunctions, and hole-free structures, are used, as shown in [Fig. II.12](#) [143]. The design of mesoporous superstructure cells (MSSCs) involves using a mesoporous semiconductor oxide layer, such as TiO_2 [148], ZnO [149], Zn_2SO_4 [150], or alumina (Al_2O_3), to reduce electron and hole recombination and improve electron transport in the perovskite layer. With a bandgap of 7–9 eV, Al_2O_3 is a wide-bandgap insulator that enhances electron transport and confers dual characteristics as a sensitizer and an n-type conductor [151].

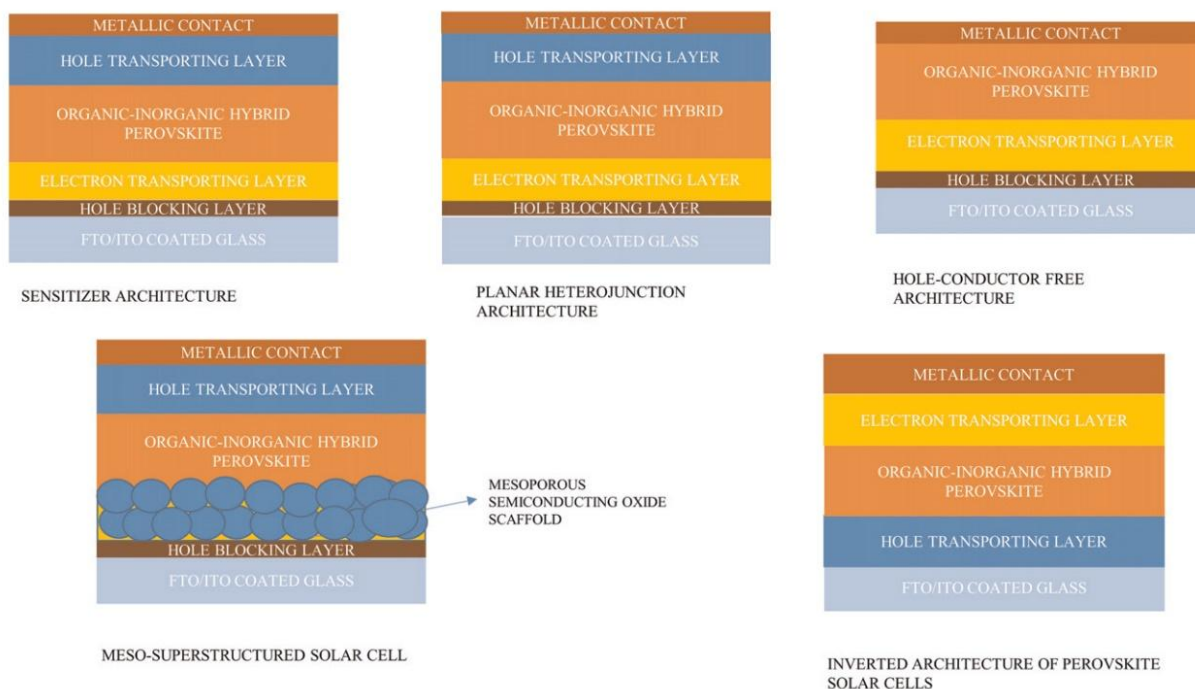


Fig. II.12: Different design of photovoltaic cells [143].

In solar cells and LEDs, charge separation and transport are facilitated by the planar heterojunction architecture, which uses flat layers of donor and acceptor materials. This design is easy to fabricate, and the interfaces can be controlled, but exciton dissociation can be less efficient than in bulk heterojunctions. Perovskite semiconductors used in p-i-n heterojunction solar cells perform the basic functions of photovoltaic systems, including light absorption, voltage generation, and electron and hole transport [143].

II.7. Manufacturing and processes

Solar cell manufacturing relies on several methods that determine the quality and efficiency. Controlling the perovskite morphology across large areas is difficult in the case of PSCs [152,153]. Therefore, it is crucial to select the manufacturing technique with great care [154,155]. The rectangular shape of thin film-based solar cells is intended to decrease the length of charge carrier transport path [156]. The most extensively documented and effective method for PSC fabrication in the scientific literature is based on solution processing. Spin coating, dip coating, doctor blade coating, spray coating, ink-jet printing, screen printing, drop casting, and slot die coating are some of the procedures used for solution-processed deposition [157].

II.7.1. Spin-coating

Spin coating is one of the most popular commonly used methods in this technology. It is the most economical, efficient, easy-to-use, and rapid method for depositing thin films on substrates, because it produces to create extremely uniform films. When the solution of a particular substance is spun at high speed, the liquid's surface tension and centripetal force combine to form a uniform layer on the substrate [158]. The process of baking the film after spin coating usually results in well-crystallised perovskite layers, which strengthen bonding and adhesion between metal cations and halogen anions [159].

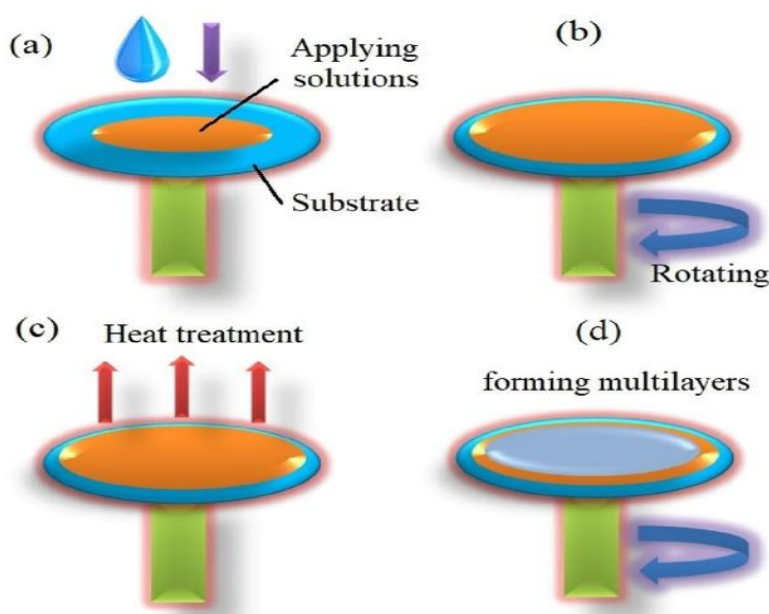


Fig. II.13: the spin coating process [160].

The spin coating starts with deposition, which involves spreading the solution on the substrate. Centrifugal force causes the solution to be pulled across the substrate surface either when the substrate is spinning during dynamic spin deposition or when it is placed on the spinner after deposition (static spin deposition) [158].

The second step is spin-up; after pouring the liquid material directly onto the substrate, it is possible to apply a direct or progressive speed that differs from the substrate speed in the first step. As a result, a smooth and uniform liquid layer surface is produced.

The third step is the spin-off; at this stage, a thin, sticky layer forms over the substrate. It should be noted that at this point, the drying process is initiated because no rotation speed is activated; instead, the drops that are dispersed on the sides are separated and removed, and the colour changes from transparent to opaque.

The final stage is evaporation. At this point, solvent drying is performed at a precise temperature and pressure that are established by prior research and vary based on the solvent used. The viscosity decreases and a thin, solid layer is formed. It should be noted that all steps of this process must be carried out in a clean and controlled environment in order to avoid the presence of impurities in the solar cells.

II.7.2. Dip coating

Dip coating is the simplest method for forming thin films on small areas. It involves immersing the substrate in a liquid containing dissolved metal compounds and then removing it from the solution in a clean atmosphere to prevent impurities from contaminating the film. Initially, a thin liquid layer forms on the substrate's surface. This layer is then dried at room temperature, producing a homogeneous thin film. *Fig. II.14* shows a schematic representation of the dip-coating method. Small nanoparticles (a few nm to a few tens of nm) can be added to the precursor sol to provide mesoporosity, or the powder can be mixed with a volatile substance such as naphthalene, hydrogen peroxide, or polymethyl methacrylate (PMMA), which when deposited in a compact, crack-free layer, produces films with pore diameters ranging from 2 to 50 nm (in accordance with the international union of pure and applied chemistry definition of mesoporosity) [161]. Dip coating is a common method for enhancing optical coatings, such as in the fabrication of automotive rearview mirrors and large-area antireflective coatings for solar glazing glasses.

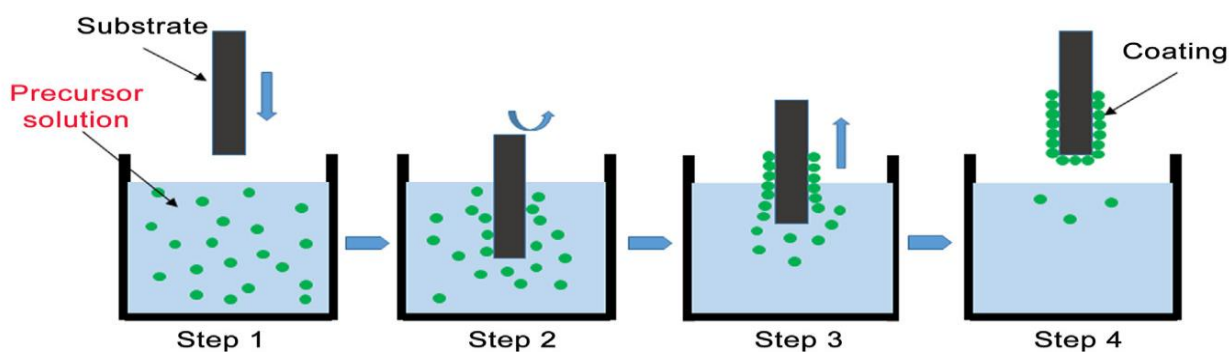


Fig. II.14: The dip-coating process [161].

II.7.3. Spray coating

Spray coating involves printing ink being forced through a nozzle, resulting in the formation of a fine aerosol [162]. Spray coating, which is a process that is industrially scalable, cost-effective, and capable of covering a large area, can be utilized to make thin films of material that conform to the substrate's shape [158]. The characteristic performance of polymer solar cells is hindered by the spray coating process due to drawbacks such as isolated droplets, a non-uniform surface, and pinholes [163,164]. The process of spray coating involves ejecting fine liquid particles of functional materials onto the substrate through a jet stream of carrier gas, and this method works well with any substrate material and is particularly suitable for processing at low temperatures [158,165]. *Fig. II.15* depicts both the commercially available airbrush spray coating apparatus and the electro-spray coating apparatus.

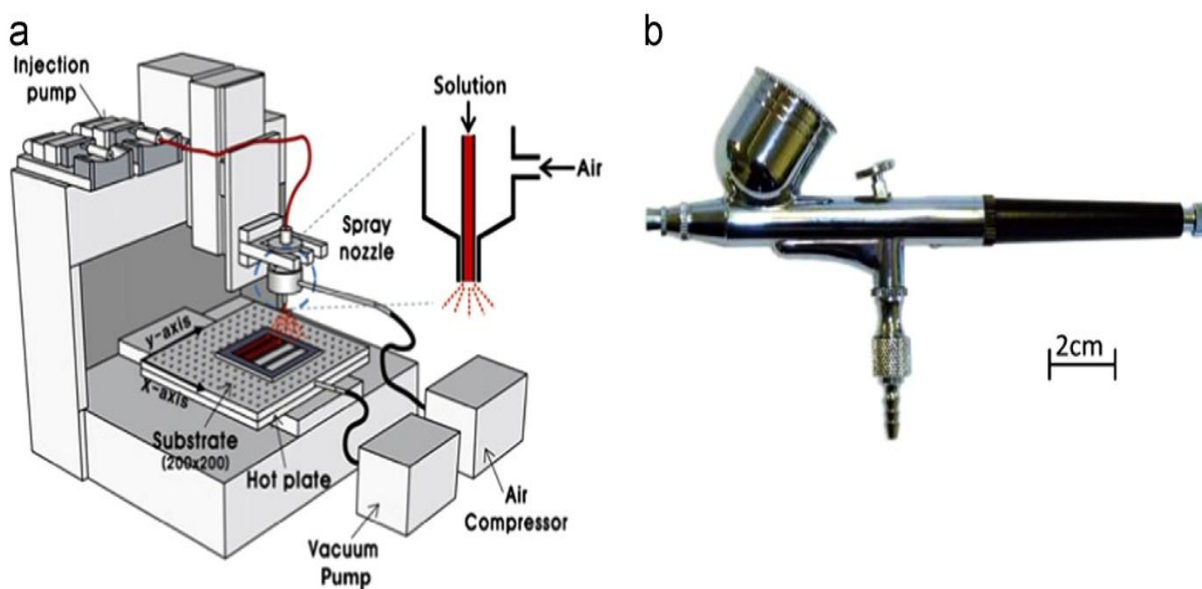


Fig. II.15: The schematic diagram of the spray-coating equipment, which includes the (a) electro-spray coater [166] and the (b) air-brush spray coater [167].

II.8. Conclusion

The evolution of photovoltaic technologies demonstrates continuous innovation aimed at improving energy conversion efficiency and reducing manufacturing costs to expand production capabilities. The emergence of the first generation of silicon-based solar cells dominated the commercial market due to their proven performance. The second generation introduced

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technologies to produce thinner and more flexible materials, including crystalline silicon, cadmium telluride, and CIGS, which enhanced the commercial market in terms of cost and efficiency. Recently, perovskite solar cells have emerged, opening new horizons in terms of efficiency, stability, and tunability. Furthermore, this section has highlighted the development of manufacturing techniques such as dip coating and spray coating, which have played a major role in advancing production.

***Chapter III: Physical
properties: calculation,
results, and discussion***

III.1. Introduction

The main goal of this work is to examine the structural, elastic, electronic, and optical properties of perovskite chalcogenides CaSiX_3 ($X=\text{S}$, Se , and Te) using density functional theory (DFT) and the FP-LAPW method. In general, the structure of this type of perovskite can undergo significant compositional changes to develop specific properties that allow the substitution of cations at sites A and/or B within the perovskite lattice. These changes contribute to the material's high performance in the visible spectrum and excellent conductivity, making it ideal for various applications, including different types of solar cells and other electro-optical detectors.

Indeed, the recently published results on this type of material have attracted most researchers' attention. However, the search for unexplored compounds remains challenging due to the rapid proliferation of both experimental and theoretical studies. This raises the question of how many remaining compounds can be thoroughly investigated and whether they will deliver the desired results while maintaining structural stability.

The simulation that we presented, a simple overview of in this chapter, based on the density function theory (DFT), offers a new view of this type of material and its properties, paving the way for future investigations and applications. We expect that our findings will inspire future research and promote their use in the green energy sector.

III.2. DFT and the FP-LAPW Method: An overview

To gain a more precise understanding of the various properties of solid materials, it is necessary to study them in depth regarding the behavior of the electrons they contain. From ancient times to the present day, traditional methods have undergone numerous modifications and developments, including the use of advanced computers. Theoretical approaches based on simplifications that make the problem easier to handle are typically employed to solve the N-body problem. As identical nuclei, these particles exhibit electromagnetic interactions. Here, quantum physics intervenes in the electronic structure, which determines the different physical properties of matter. The form of the Schrödinger equation is contingent upon the physical context. Nonetheless, the time-dependent Schrödinger equation, which describes a system evolving over time (t), represents the broadest interpretation [168].

$$H_{tot}\psi(\vec{r}_i;t) = E\psi(\vec{r}_i;t) \quad (\text{III.1})$$

With ψ as the quantum system's wave function, and H as the Hamiltonian operator. Within this system, the accurate many-particle Hamiltonian consists of the kinetic energy of the nuclei T_N , the kinetic energy of the electrons T_e , and the interaction terms: the interaction between the nuclei V_{N-N} , the interaction between electrons V_{e-e} , and the nuclei-electrons interaction V_{N-e} .

$$H_{tot} = T_N + T_e + V_{N-N} + V_{e-e} + V_{N-e} \quad (\text{III.2})$$

The emergence of the full-potential linear augmented plane wave (FP-LAPW) method has had a significant impact on the simulation of the electronic properties of materials based on density functional theory (DFT). Density functional theory, or DFT for short, is based on two fundamental theorems: it describes a physical characteristic of individual materials based on density without taking into account position, and use the real ground-states density to minimize total energy [169,170].

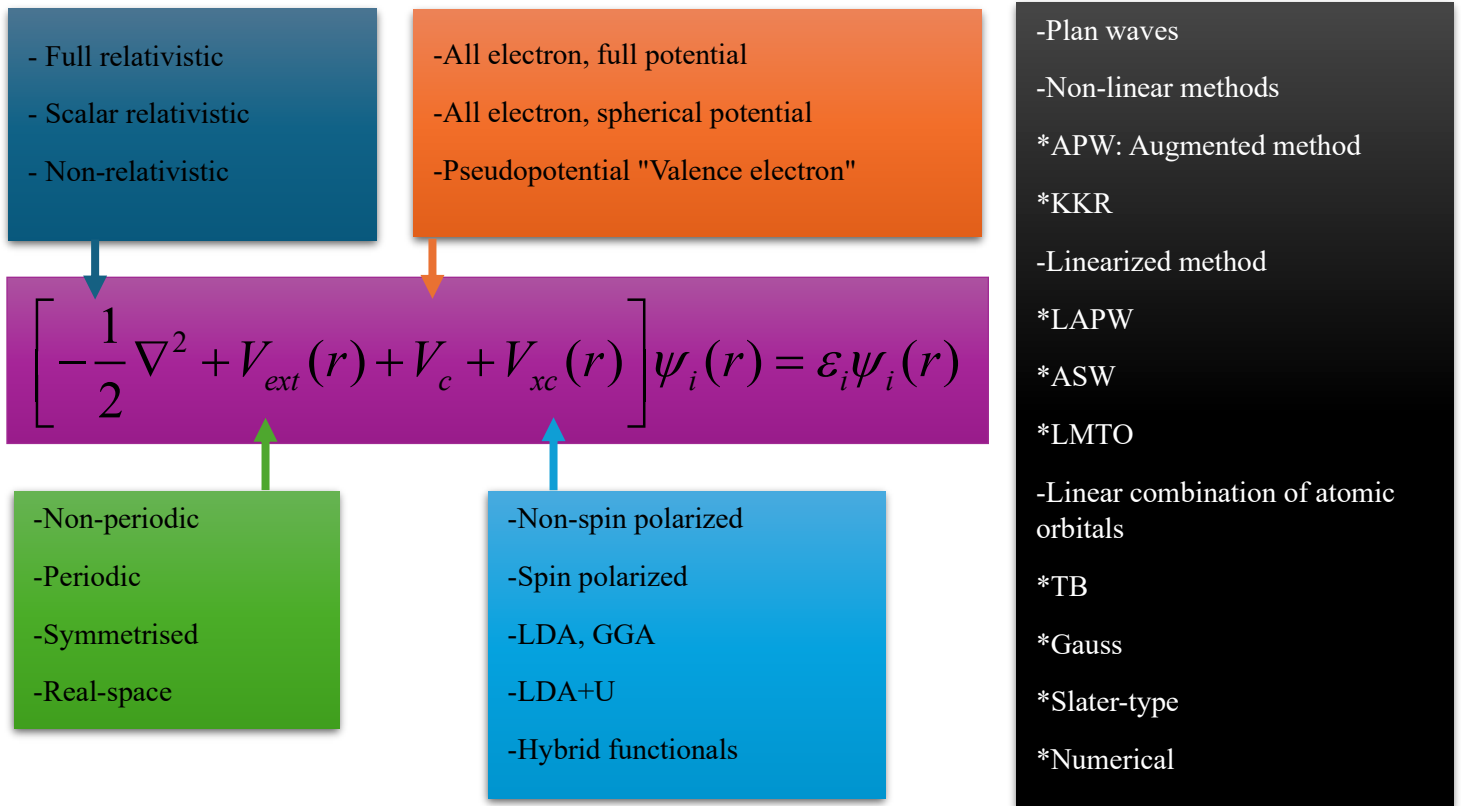
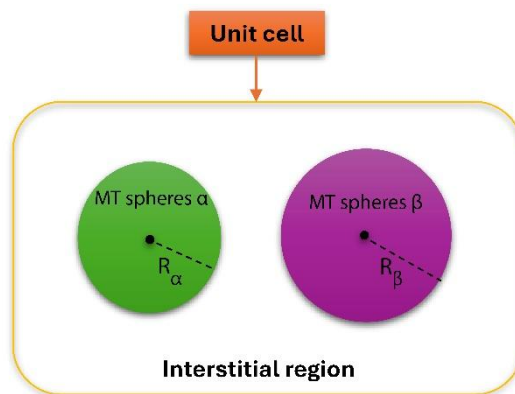


Fig. III.1: An overview of computations for electronic structures [171].

III.3. The FP-LAPW Methode: A Comprehensive Overview

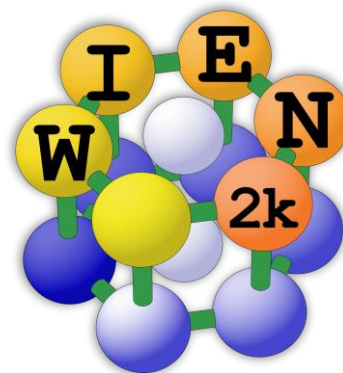
Slater first proposed the APW formulation in 1937[172,173]. The potential and wave functions around an atomic nucleus are almost spherical and strongly varying, just as those in an atom. On the other hand, the potential and wave functions are smoother in the interstitial region between the atoms. At the determined eigenvalues, the plane waves are matched to the Schrödinger equation's precise solutions at the MT sphere surface [174,175]. During the ab initio computation, the unit cell was divided into non-overlapping muffin-tin (MT) spheres, and the interstitial region occupied the remainder of the space. Because it results in a non-linear eigenvalue problem and an explicit energy dependence of the basic functions (and hence of the overlap and Hamiltonian matrices), this method is computationally costly.



In our calculations, $K_{\max} = 7/R_{\text{MT}}$ was chosen (where the vector wave K has a maximum value called $K_{\max}$ and the average radius of the spherical muffin tin is known as R_{MT} , which relies on the selected atoms of the compound). The valence wave functions in the muffin-tin spheres were enlarged up to $l_{\max} = 10$, whereas the Fourier expansion of the charge density was restricted to $G_{\max} = 12 \text{ a.u.}^{-1}$. We used $10 \times 10 \times 10$ k-points meshes in the irreducible wedge of the Brillouin zone. The smallest muffin-tin radii (R_{MT}) for Ca, Si, S, Se, and Te are 1.9, 1.8, 1.8, 1.9, and 2.25 Bohr, respectively.

III.4. WIEN2K Code

Based on the full-potential linearized augmented plane wave (FP-LAPW) approach within the context of density functional theory (DFT), WIEN2k is a computational module. Developed by Karlheinz Schwarz and Peter Blaha, this code [24,176] consists of several individual applications linked through a C-SHELL script, and it has been very successful in condensed matter physics research due to its ease of use and comprehensive user guide [177]. Additionally, it is commonly employed in modeling complex crystalline structures. High precision is also achieved in calculating various characteristics,



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including optical, magnetic, electrical, and structural properties. Furthermore, terminology for relativistic corrections is utilized [178]:

- ✚ The Darwin correction and the mass-velocity correction are scalar-relativistic adjustments.
- ✚ The correction for spin-orbit coupling.

Utilizing this kind of software entails a number of fundamental procedures that rely on selecting a set of fundamental variables that impact the precision of the outcomes Ref [177] allows for a more precise understanding.

III.5. Results and discussion

III.5.1. Structural properties

In order to study and analyze the geometric design of the compounds, we created a file containing the detailed structure of each compound (Case.struct), including the distribution of atoms. The three compounds are characterized by a similar overall distribution of atoms, while the difference lies in the type of the third atom in each compound within the general formula CaSiX_3 , where X represents S, Se, or Te. All this was done using the interface of the WIEN2K code [179].

We employed the Full-Potential Linearized Augmented Plane Wave (FP-LAPW) method combined with the Generalized Gradient Approximation (GGA) for the density functional. All lattice parameters and atomic positions were refined by minimizing the forces acting on the atoms using the GGA method [180].

Utilizing these techniques, we precisely identified the parameters defining the fundamental state structure of the CaSiX_3 (X= S, Se, and Te) compounds, in the orthorhombic phase with a Pnma space group (N°62). **Fig. III.2** illustrates the geometrical crystal structure of the compounds studied using VESTA, and the distances between atoms are shown in **Table III.1**.

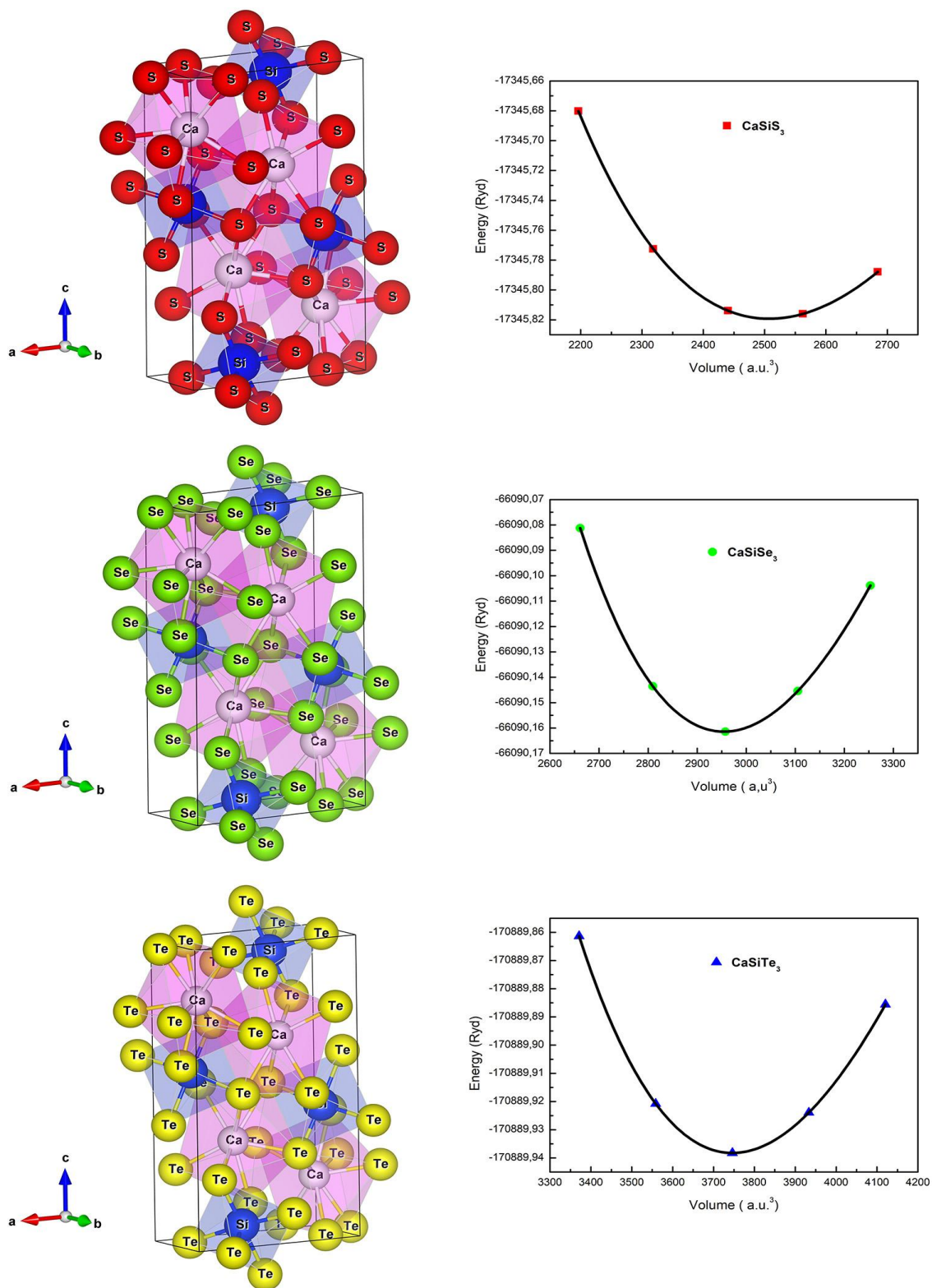


Fig. III.2: The crystal structure of CaSiX_3 ($\text{X}=\text{S}$, Se , and Te) exhibits an orthorhombic arrangement and belongs to the Pnma space group (N° . 62).

Table III.1: Minimum interatomic distances within the CaSiX₃ composite (where X = S, Se, and Te) in angstroms (Å) and tolerance factor (t).

	CaSiS ₃	CaSiSe ₃	CaSiTe ₃
Ca-Ca (Å)	4.39744	4.62149	4.88085
Ca-Si (Å)	4.06294	4.29825	4.52342
Ca-X (Å)	3.31295	3.42295	3.46598
Si-Si (Å)	6.52787	6.88374	7.22770
Si-X (Å)	2.47602	2.61002	2.84002
<i>t</i>	0.726	0.726	0.725

The presence of numerous crystallographic databases characterizes the crystal lattice. These databases are rich in information and provide the ionic radii and atomic radii present in a crystal for all chemical elements. Additionally, they account for variations in charges and coordination [181,182].

The Goldschmidt tolerance factor (*t*) [183] is a reliable numerical criterion used to assess structural steady states and the deformation of materials such as perovskites. The following expression can be used to calculate the Goldschmidt tolerance factor based on the ionic radius of the atoms [183,184], where R_{Ca} , R_{Si} , R_S , and R_{Se} denote the radii of the atoms in the compounds

$$t = \frac{(R_{Ca} + R_{S/Se})}{\sqrt{2}(R_{Si} + R_{S/Se})} \quad (III.3)$$

According to many published data, this coefficient is assumed to lie between 0.9 and 1 for the cubic case, if it exceeds this value, the phase is hexagonal, while if it is less than 0.9, the phase is orthorhombic or rhombohedral [185,186]. The tolerance factor values are listed in [Table III.1](#). A high tolerance factor of 0.726 for both CaSiS₃ and CaSiSe₃, and 0.725 for CaSiTe₃, confirms the orthorhombic stability of these perovskites.

The structural optimization assessment procedure requires the identification of the minimum total energy. This task is performed using the Murnaghan equation of state ([Eq. III.4](#)) [187–190]. The application of this equation is based on the analysis of the calculated data. This information is

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crucial for determining essential parameters such as the equilibrium lattice constant, the bulk modulus, and its first derivatives. (E_0 and V_0 represent, respectively, the total energy and the volume at equilibrium when pressure and temperature are zero).

$$E(V) - E(V_0) = \frac{B_0 V}{B'_0} \left[\frac{(V_0 / V)^{B'_0}}{B'_0} + 1 \right] - \frac{B_0 V_0}{B'_0 - 1} \quad (\text{III.4})$$

In a crystalline structure, where potential energy is minimized, the edge length of the unit cell is linked to the lattice constant (parameters a , b , c) at equilibrium. The modulus of elasticity measures a material's resistance to uniform compression (B), and its first derivative (B') provides information about the pressure dependence of this modulus. The graph that representing energy versus volume of CaSiX_3 compounds ($X = \text{S, Se and Te}$) shown in [Fig. III.2](#). Notably, CaSiTe_3 has a lower compressibility modulus (B) value of 49.2733 GPa compared with CaSiSe_3 (66.7110 GPa) and CaSiS_3 (83.5423 GPa), as shown in [Table III.2](#). This table also illustrates that when the sulfur atom (S) is substituted by a selenium (Se) or tellurium (Te), the lattice constants (a , b , and c) increase, while the compressibility modulus B decreases with percentages of 25.23% and 69.54% ($\frac{B_{\text{CaSiS}_3} - B_{\text{CaSiSe}_3/\text{CaSiTe}_3}}{B_{\text{CaSiSe}_3/\text{CaSiTe}_3}} \times 100$). This variation is due to the difference in atomic number Z

between sulfur, selenium, and tellurium atoms, with atomic numbers 16, 34, and 52, respectively. Therefore, they have different electronic configurations, which are detailed in [Table III.3](#). These configurations influence the properties of each material. However, the compressibility modulus exhibits an opposite behavior, it decreases when the atomic number Z of the atom increases [191]. In addition, the energy values indicate that CaSiTe_3 has lower energy, with value of -170889.9382 Ryd, against -66090.16135 Ryd for CaSiSe_3 and -17345.81928 Ryd for CaSiS_3 (see [Table III.2](#)).

The formation energy, ΔH_f , is an essential parameter to determining the thermodynamic stability of compounds. This energy is calculated by combining two main components: the energy of the compound and the energy associated with the individual atoms that make them up. A negative value of ΔH_f (i.e., $\Delta H_f < 0$) indicates stability in the compound. Conversely, a positive value of ΔH_f (i.e., $\Delta H_f > 0$) indicates low stability or instability in the compound. It can be calculated using the following equation:

$$\Delta H_f = E_{\text{Tot}} - (E_{\text{Ca}} + E_{\text{Si}} + 3E_{\text{S/Se/Te}}) \quad (\text{III.5})$$

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In a relaxed state, the energy of the compound denoted as E_{Tot} , and the energy of each atom in the compound, represented as E_A , E_B , and E_X , are considered. CaSiS_3 exhibits high thermodynamic stability with a value of -39.366 eV, more than CaSiSe_3 of -25.399 eV, and CaSiTe_3 of -13.987 eV ([Table III.2](#)).

Table III.2: Structural parameters and enthalpy of formation ΔH_f calculated using the PBE-GGA approximation for CaSiS_3 , CaSiSe_3 , and CaSiTe_3 .

	Lattice constant (Å)			$B(\text{GPa})$	B'	E_0 (Ryd)	ΔH_f (eV)
	a	b	c				
CaSiS₃	7.9108	3.5434	13.2602	83.5423	4.1704	-17345.81928	-39.3664
CaSiSe₃	8.3016	3.7613	14.0223	66.7110	4.4639	-66090.16135	-25.3993
CaSiTe₃	8.7694	4.1375	15.3013	49.2733	4.5357	-170889.9382	-13.9873

Table III.3: The electronic configuration of the elements involved in the composition of the materials analyzed.

Ca [Ar] s^2	Si [Ne] $3s^2 3p^2$	S [Ne] $3s^2 3p^4$
Se [Ar] $3d^{10} 4s^2 4p^4$	Te [Kr] $4d^{10} 5s^2 5p^4$	

III.5.2. Stability Analysis

In this section, we have presented an in-depth study of the physical properties related to the stability of compounds and their constituent atoms by analyzing the elastic properties and phonon frequencies. This approach opens the door to the potential industrial production of these materials in the case of the complete compound stability.

III.5.2.1. Elastic Attributes

The elastic constant is necessary to determine the mechanical properties of any material and to demonstrate its response to external forces. This theory connects the mechanical and dynamic characteristics of materials [192]. Insights into the stiffness, anisotropy, and structural stability of the material can be obtained from its elastic properties, which also shed light on the interconnection

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between neighboring atomic levels [193,194]. In addition, the understanding of the structural stability and mechanical properties of a crystal is greatly enhanced by analyzing its elastic constants [195]. **Table III.4** presents the elastic constants calculated at room temperature. Mechanical stability criteria are defined based on the following conditions [196] :

$$C_{ii} > 0 \quad (1 \sim 6) \quad (\text{III.6})$$

$$C_{ii} + C_{jj} - 2C_{ij} > 0 \quad (\text{III.7})$$

$$C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0 \quad (\text{III.8})$$

The determined elastic constants for CaSiX_3 ($X = \text{S, Se, and Te}$) comply with all the aforementioned equations, confirming their physical stability. We can state that they are mechanically stable, and the values of the elastic constants are high since $C_{ij} > 20$ GPa, which indicates that the material is not loose and that if small pressures are exerted on the crystals in any direction, the total energy changes and is redistributed to prevent distortions.

The elastic constants C_{44} , C_{55} , and C_{66} measure resistance to shear distortions, which are essential for mechanical stability [197,198]. Higher values indicate stronger resistance to deformation. Similarly, the constants C_{11} , C_{22} , and C_{33} indicate the material's resistance to compressive strains. **Table III.4** shows that shear deformation resistance is much lower than compressional deformation resistance. It is noted that the values of this resistance decrease when the third atom of the compound is changed; the presence of sulfur (S) yields the high values of $C_{11} = 145.4557$, $C_{22} = 159.4213$, and $C_{33} = 169.8420$ GPa; selenium (Se) gives $C_{11} = 113.2858$, $C_{22} = 121.7968$, and $C_{33} = 124.1412$ GPa; while tellurium (Te) results in the lower values of $C_{11} = 77.9278$, $C_{22} = 88.2008$, and $C_{33} = 90.769$. The main cause of these decreases is likely the same factor responsible for the reduction in the constants observed in the structure study, namely the difference in electronic configuration.

We can see that C_{23} has the lowest value among the rest of the constants 44.0452 GPa for $X = \text{S}$, 32.6552 GPa for $X = \text{Se}$, and 23.0125 GPa for $X = \text{Te}$. In contrast, but C_{33} has the highest value than C_{22} and C_{11} . This ordering means the atomic bonding between nearest neighbors is stronger along the (001) planes than along the (010) and (100) planes.

Table III.4: The elastic constant calculated for CaSiS₃, CaSiSe₃, and CaSiTe₃ obtained from the PPE-GGA.

C_{ij} (GPa)	<i>CaSiS₃</i>	<i>CaSiSe₃</i>	<i>CaSiTe₃</i>
C_{11}	145.4557	113.2858	77.9278
C_{22}	159.4213	121.7968	88.2008
C_{33}	169.8420	124.1412	90.7690
C_{44}	40.8276	30.3076	21.1891
C_{55}	66.7377	28.9507	12.1163
C_{66}	50.1138	38.1329	28.4144
C_{12}	49.5052	45.9557	46.4259
C_{13}	58.4901	46.2569	31.4675
C_{23}	44.0452	32.6552	23.0125

III.5.2.1.1. Bulk's modulus (*B*)

One of the most important properties to know about a solid substance is its bulk modulus, denoted as *B*. This modulus is used to measure the material's resistance to uniform compression applied along the edge of the structure's axes against volume changes [199,200]. The Voigt (B_V), Reuss (B_R), and Hill (B_H) bulk modulus can be calculated using [Eq. III.9](#), [III.10](#), and [III.11](#), respectively [201–203].

The best resistance was observed to be for CaSiS₃ with a Bulk's value of $B_V = 86.533$, $B_R = 86.288$, and $B_H = 86.410_H$ GPa. In comparison, CaSiSe₃ shows values of $B_V = 67.662$, $B_R = 67.641$, and $B_H = 67.651_H$ GPa. CaSiTe₃ exhibit the lowest resistance, with values of $B_V = 50.967$, $B_R = 50.822$, and $B_H = 50.894$ GPa.

$$B_R = \frac{1}{(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})} \quad (\text{III.9})$$

$$B_V = \frac{1}{9}(C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23}) \quad (\text{III.10})$$

$$B_H = (B_R + B_V) / 2 \quad (\text{III.11})$$

III.5.2.1.2. Shear's modulus (*G*)

This orthorhombic structure has a lower shear stress durability than the volumetric deformation, as its shear's modulus (denoted as *G*) is lower than the calculated bulk modulus (see

Table III.5). It is defined as the ratio of shear stress and shear strain [204], the Voigt shear Reuss shear and Hill shear modulus (G_V , G_R , and G_H) can effortlessly be computed from the [Eq. III.12](#), [III.13](#), and [III.14](#). The values of these moduli can be arranged for comparison among the three compounds as follows $G_{CaSiS_3} > G_{CaSiSe_3} > G_{CaSiTe_3}$. The presence of sulfur (S) gives $G_V = 53.046$, $G_R = 51.418$, and $G_H = 52.232$ GPa. In contrast to the presence of tellurium (Te), yields lower values of $G_V = 22.742$, $G_R = 19.885$, and $G_H = 21.313$ GPa. Selenium (Se) in the structure gives intermediate values of $G_V = 35.101$, $G_R = 34.186$, and $G_H = 34.643$ GPa.

$$G_V = \frac{1}{15}(C_{11} + C_{22} + C_{33} - C_{12} - C_{13} - C_{23}) + 3(S_{44} + S_{55} + S_{66}) \quad (III.12)$$

$$G_R = \frac{15}{4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})} \quad (III.13)$$

$$G_H = (G_R + G_V) / 2 \quad (III.14)$$

For a better understanding, we have plotted this modulus using the ELATools code[205] in [Fig. III.3, III.4, and III.5](#), which allows us to visualize it directly in both 2D and 3D, along with its projections on the $\langle XY \rangle$, $\langle XZ \rangle$, and $\langle YZ \rangle$ planes. These plots were generated using the values of the elastic constants (C_{ij}) calculated from the stiffness matrix:

$$C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{pmatrix} \quad (III.15)$$

$$C_{ij}(CaSiS_3) = \begin{pmatrix} 145.4557 & 49.5052 & 58.4901 & 0 & 0 & 0 \\ 49.5052 & 159.4213 & 44.0452 & 0 & 0 & 0 \\ 58.4901 & 44.0452 & 169.8420 & 0 & 0 & 0 \\ 0 & 0 & 0 & 40.8276 & 0 & 0 \\ 0 & 0 & 0 & 0 & 66.7377 & 0 \\ 0 & 0 & 0 & 0 & 0 & 50.1138 \end{pmatrix} \quad (III.16)$$

$$C_{ij}(\text{CaSiS}_3) = \begin{pmatrix} 145.4557 & 49.5052 & 58.4901 & 0 & 0 & 0 \\ 49.5052 & 159.4213 & 44.0452 & 0 & 0 & 0 \\ 58.4901 & 44.0452 & 169.8420 & 0 & 0 & 0 \\ 0 & 0 & 0 & 40.8276 & 0 & 0 \\ 0 & 0 & 0 & 0 & 66.7377 & 0 \\ 0 & 0 & 0 & 0 & 0 & 50.1138 \end{pmatrix} \quad (\text{III.16})$$

$$C_{ij}(\text{CaSiSe}_3) = \begin{pmatrix} 113.2858 & 45.9557 & 46.2569 & 0 & 0 & 0 \\ 45.9557 & 121.7968 & 32.6552 & 0 & 0 & 0 \\ 46.2569 & 32.6552 & 124.1412 & 0 & 0 & 0 \\ 0 & 0 & 0 & 30.3076 & 0 & 0 \\ 0 & 0 & 0 & 0 & 28.9507 & 0 \\ 0 & 0 & 0 & 0 & 0 & 38.1329 \end{pmatrix} \quad (\text{III.17})$$

$$C_{ij}(\text{CaSiTe}_3) = \begin{pmatrix} 77.9278 & 46.4259 & 31.4675 & 0 & 0 & 0 \\ 46.4259 & 88.2008 & 23.0125 & 0 & 0 & 0 \\ 31.4675 & 23.0125 & 90.7690 & 0 & 0 & 0 \\ 0 & 0 & 0 & 21.1891 & 0 & 0 \\ 0 & 0 & 0 & 0 & 12.1163 & 0 \\ 0 & 0 & 0 & 0 & 0 & 28.4144 \end{pmatrix} \quad (\text{III.18})$$

III.5.2.1.3. Young's modulus (E)

In addition, the stiffness of the material is calculated using Young's modulus (E) (Voigt, Reuss, and Hill), which describes its non-uniform relative strain [206]. This modulus can be defined in three dimensions, as shown in [Fig. III.3, III.4, and III.5](#) for CaSiX_3 ($X=\text{S}$, Se , and Te). If this modulus can form a perfect sphere, it indicates the material is isotropic, meaning that its physical properties are uniform in all directions. In contrast, crystals exhibit anisotropy, where these properties can vary based on direction. The degree of divergence of the three-dimensional Young's modulus from a sphere can be interpreted as a measure of anisotropy, which has been observed in the behavior of these anisotropic materials. Therefore, the deviation degree can reflect the anisotropy degree of a crystal [207]. Using the Zener ratios (A_1 , A_2 , and A_3), it is possible to quantify the elastic anisotropy of an orthorhombic crystal using the following relationship [202]:

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \quad (III.19)$$

$$A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}} \quad (III.20)$$

$$A_3 = \frac{4C_{66}}{C_{11} + C_{22} + 2C_{12}} \quad (III.21)$$

The ratios of the Zener coefficients are given in [Table III.5](#), where they represent the percentage of variance anisotropy A_1 , A_2 , and A_3 according to the shear planes (100), (010), and (001), respectively. Young's modulus (E) can be calculated from the Shear's modulus (G) using the following relationship:

$$E_V = \frac{9B_V G_V}{3B_V + G_V} \quad (III.22)$$

$$E_R = \frac{9B_R G_R}{3B_R + G_R} \quad (III.23)$$

$$E_H = \frac{9B_H G_H}{3B_H + G_H} \quad (III.24)$$

III.5.2.1.4. Pugh (B/G) and Poisson's ratio (σ)

Pugh introduced the ductility ratio (B/G) (Voigt, Reuss, and Hill) [200] to evaluate compound ductility straightforwardly. If $(B/G) > 1.75$, the compound is considered ductile (flexible); otherwise, it is brittle. When discussing ductile solids, Poisson's ratio σ typically takes on values greater than 0.26, For CaSiSe_3 and CaSiTe_3 we conclude that they are ductile, since $B/G > 1.75$ and $\sigma > 0.26$. In contrast, CaSiS_3 is classified as brittle, with $B/G < 1.75$ and $\sigma < 0.26$ ([Table III.5](#)). these results were visualized in both 3D and 2D projection in [Fig. III.3](#), [III.4](#), and [III.5](#).

The type of crystal bond can be determined by the Poisson coefficient (Voigt, Reuss, and Hill). For covalent materials, Poisson's ratio is approximately 0.1; for ionic materials, it is around 0.25; and for metallic materials, it is close to 0.33 [208]. CaSiS_3 and CaSiSe_3 exhibit ionic bonding, as indicated by their estimated Poisson coefficients ($\sigma \geq 0.25$). Additionally, CaSiTe_3 shows metallic bonding, with $\sigma \leq 0.33$. Poisson's ratio, σ , for anisotropic orthorhombic materials, is given by the following relationship:

$$\sigma = \frac{3B - 2G}{2(3B + G)} \quad (III.25)$$

Table III.5: The calculated bulk's modulus, shear's modulus, young's modulus, pugh ratio, and elastic anisotropy

	CaSiS ₃	CaSiSe ₃	CaSiTe ₃
B_V (GPa)	86.533	67.662	50.967
B_R (GPa)	86.288	67.641	50.822
B_H (GPa)	86.410	67.651	50.894
G_V (GPa)	53.046	35.101	22.742
G_R (GPa)	51.418	34.186	19.885
G_H (GPa)	52.232	34.643	21.313
E_V (GPa)	132.137	89.778	59.392
E_R (GPa)	128.691	87.771	52.772
E_H (GPa)	130.418	88.775	56.106
σ_V	0.245	0.278	0.305
σ_E	0.251	0.283	0.326
σ_H	0.248	0.281	0.316
T_D (K)	526.112 ± 300	324.495 ± 300	218.745 ± 300
B_V/G_V	1.6313	1.9276	2.2411
B_R/G_R	1.6782	1.9786	2.5558
B_H/G_H	1,6543	1.9528	2,3879
A_1	0.8235	0.8366	0.8014
A_2	1.1069	0.6411	0.3646
A_3	0.9737	1.0654	1.5511

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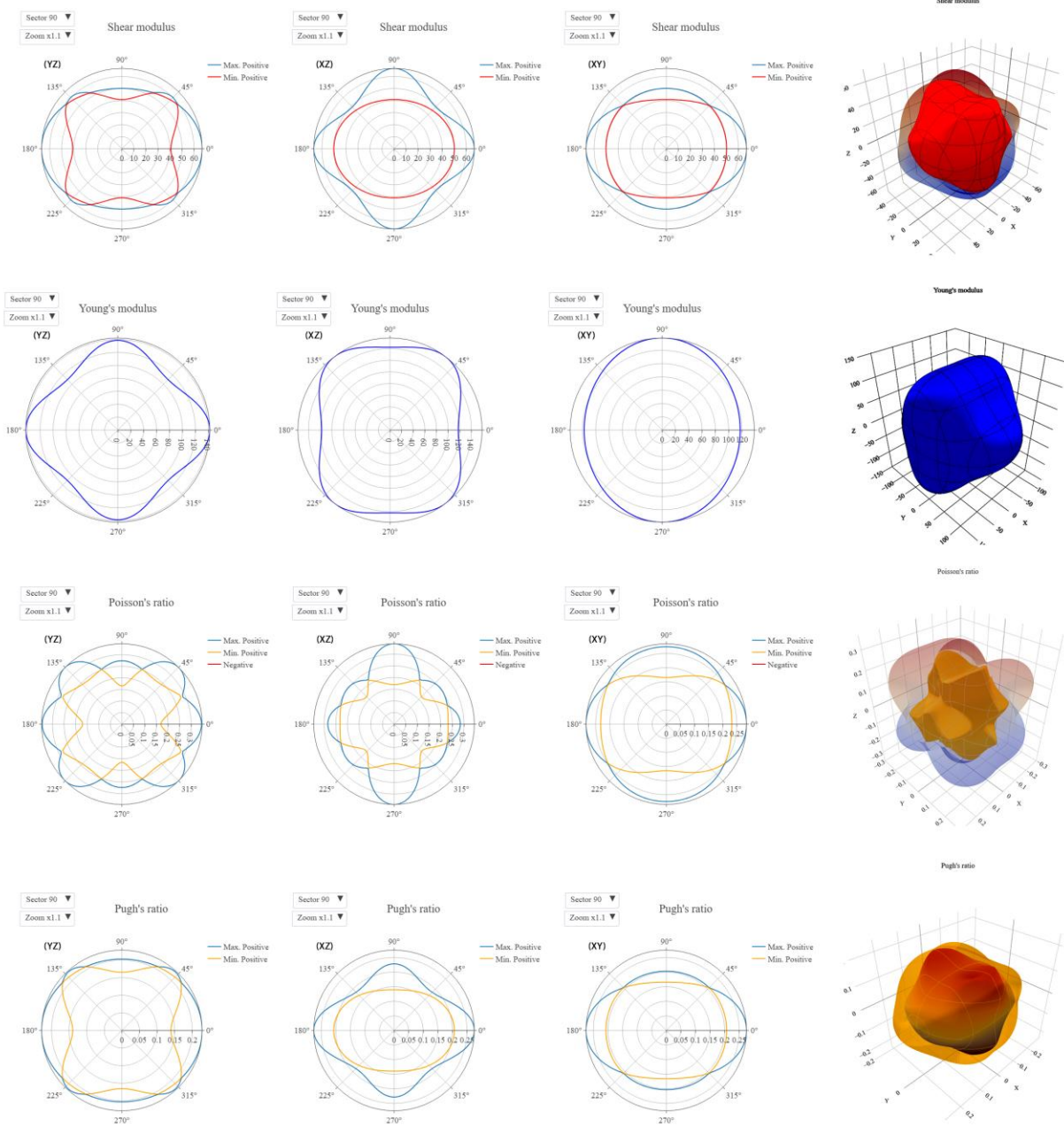


Fig. III.3: The young's modulus, shear constant and poisson's ration of CaSiS_3 are represented in 2D and 3D.

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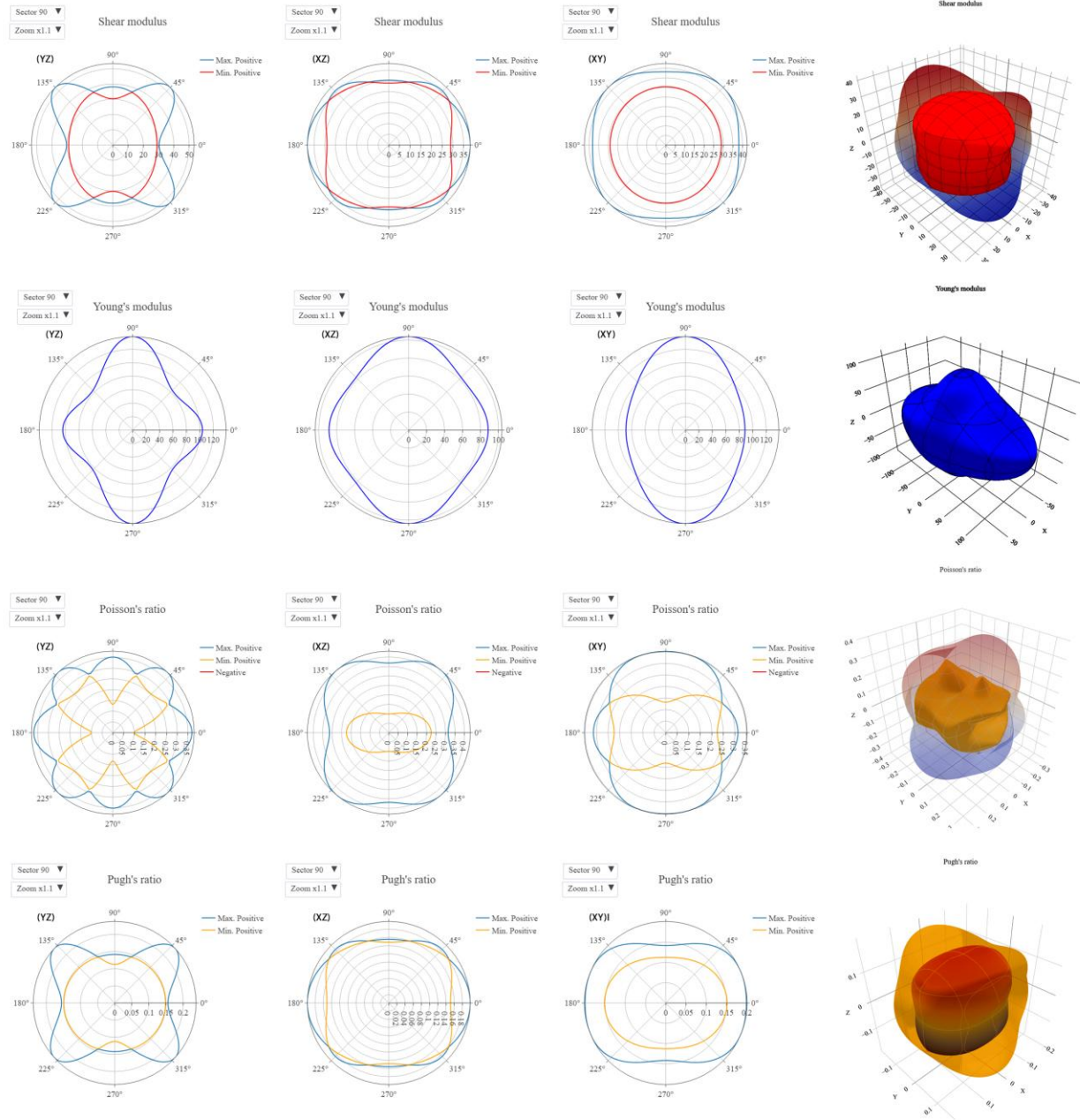


Fig. III.4: The young's modulus, shear constant and poisson's ration of CaSiSe_3 are represented in 2D and 3D.

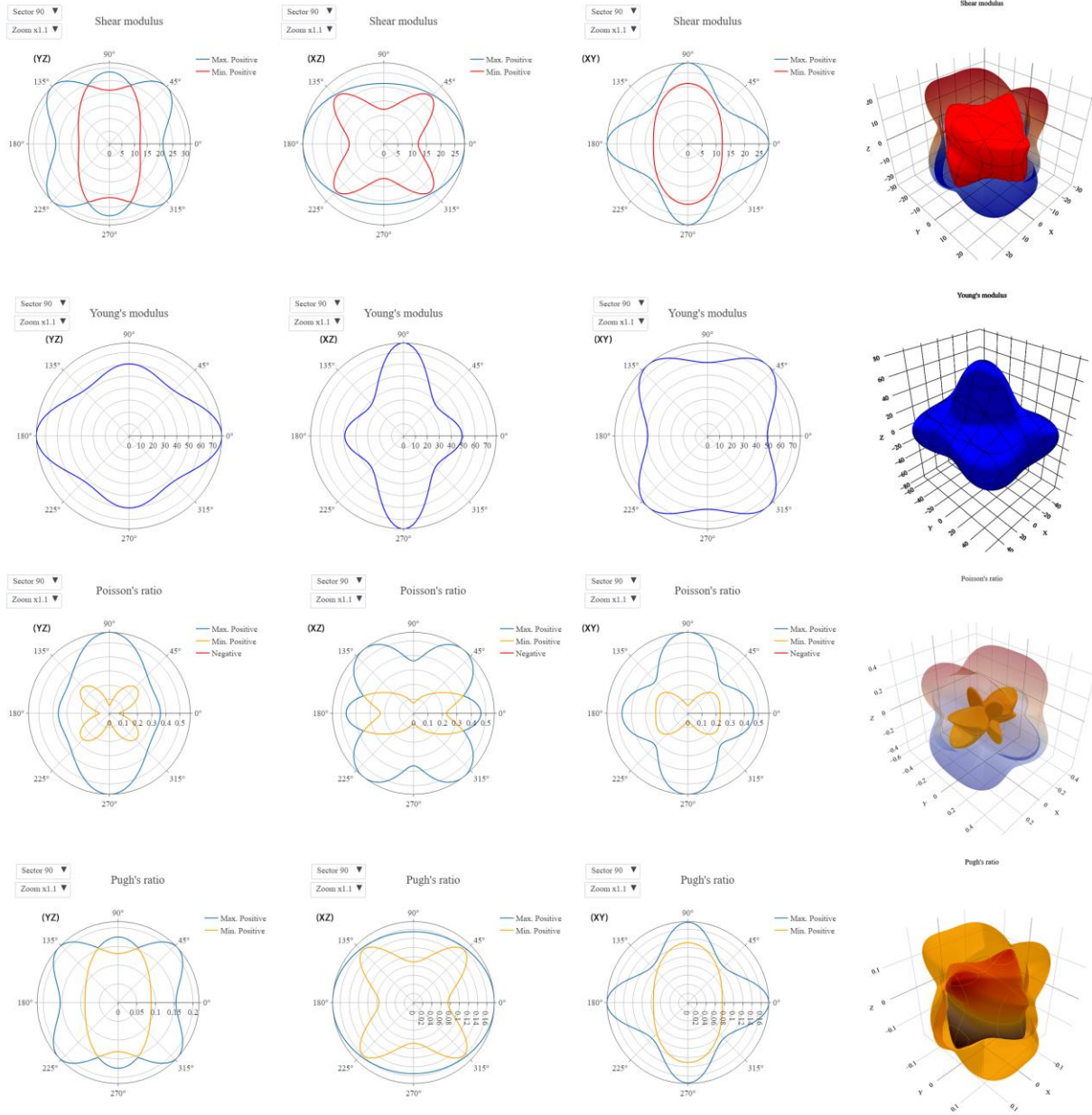


Fig. III.5: The young's modulus, shear constant and poisson's ration of CaSiTe_3 are represented in 2D and 3D.

III.5.2.2. Phonon Frequencies

In this section, we performed calculations using a $2 \times 2 \times 1$ supercell and a $30 \times 30 \times 30$ wavevector grid. **Fig. III.6** displays the phonon dispersion of CaSiX_3 ($X = \text{S}, \text{Se}, \text{and Te}$) at room temperature (300 K), calculated using the PBE-GGA exchange-correlation functional [209]. In

solid crystals, phonons determine the lattice stability through collective vibrations, which in turn govern the mechanical and thermal properties of the structure [210–212].

The phonon spectrum along the high symmetry path of the Brillouin zone is shown in [Fig. III.6 \(a, b\)](#), including the projected phonon density of states (PhDOS). Notably, the entire spectrum does not exhibit any imaginary phonon frequencies for CaSiS_3 and CaSiSe_3 , indicating that all these chalcogenide perovskites in their orthorhombic structures are dynamically stable. Therefore, their optical phonon modes are coupled with their acoustic modes. Acoustic modes include three branches that originate from zero frequency at the Γ point, with one rising more steeply and the other two more gradually. These vibrations involve collective atomic motions, similar to sound waves. Optical modes are all phonon branches above the acoustic ones, occurring at frequencies above approximately 2 THz in this system. They retain non-zero frequencies at the Γ point and are classified into low- and high-frequency optical modes based on atomic vibrations within the unit cell. In other words, optical modes are the branches above the acoustic modes with non-zero frequencies at Γ . Due to their proximity, it's inferred that the energy required to excite optical phonons is similar to that for acoustic phonons, causing their modes to overlap or merge.

The existence of imaginary values resulted in instability in the CaSiTe_3 , as shown in [Fig. III.6 \(c\)](#). Some scientists believe this is due to intrinsic limitations in the method itself. However, in this case, the values of the formation energy and the elastic constant coefficients confirm the compound's stability, suggesting that the SCAILD method is not problematic. It should be taken into account that the appearance of imaginary frequencies does not directly indicate that the materials are structurally unstable. Several hypotheses have been proposed to explain the occurrence of imaginary values, the most important being internal deformations or phase transitions induced by changes in temperature and pressure [213].

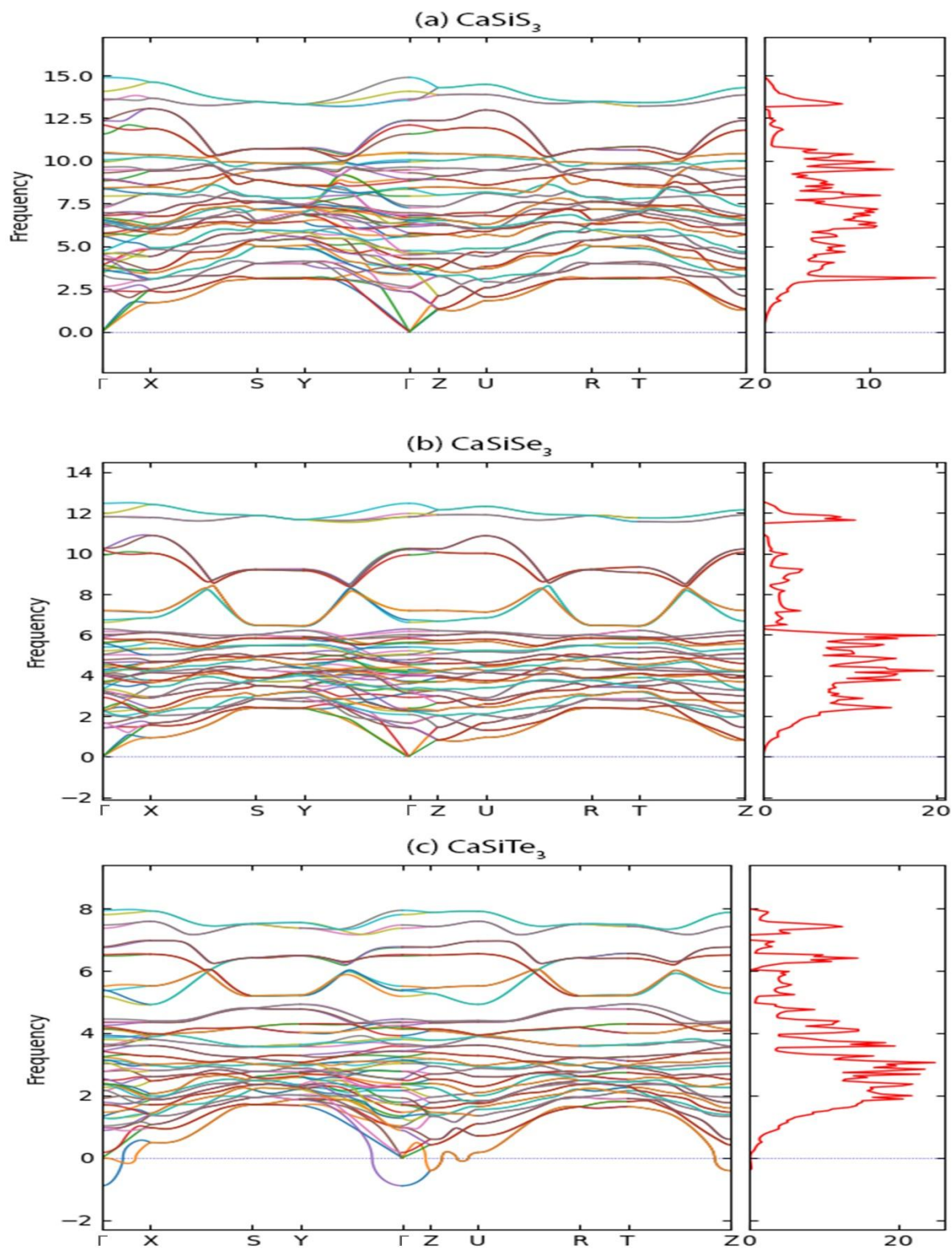


Fig. III.6: The phonon dispersion analysis of orthorhombic perovskite chalcogenide CaSiX_3 ($\text{X}=\text{S}$, Se , and Te) using PBE-GGA functional.

III.5.3. Electronic Properties

Our goal is to examine the electronic characteristics in the context of this study. To completely understand solid material characteristics, one must have a thorough understanding of electronic structure theory. Understanding how electrons behave is essential to studying these materials. The deviations in the energy bands and the overall band structure behavior can be more precisely determined thanks to this kind of study. It provides details about the occupied and unoccupied electronic states within the bands, offering insight into the material's conductivity and optical properties [214].

III.5.3.1. Electronic Structure

The detailed analysis of the electronic band structure of CaSiX_3 ($X = \text{S, Se, or Te}$) compounds is crucial. This study makes it possible to predict their potential for use in various optoelectronic devices. Specifically, it can help determine their efficiency and performance as active materials in solar cells, which is essential for the advancement of renewable energy technologies. Using FP-LAPW calculations, the electronic band structure of these compounds was examined with both the PBE-GGA and TB-mBJ methods. The band structures were calculated along the highly-symmetry path of the Brillouin zone (BZ): $\Gamma - X - S - Y - \Gamma - Z - U$ (see [Fig. III.7](#)).

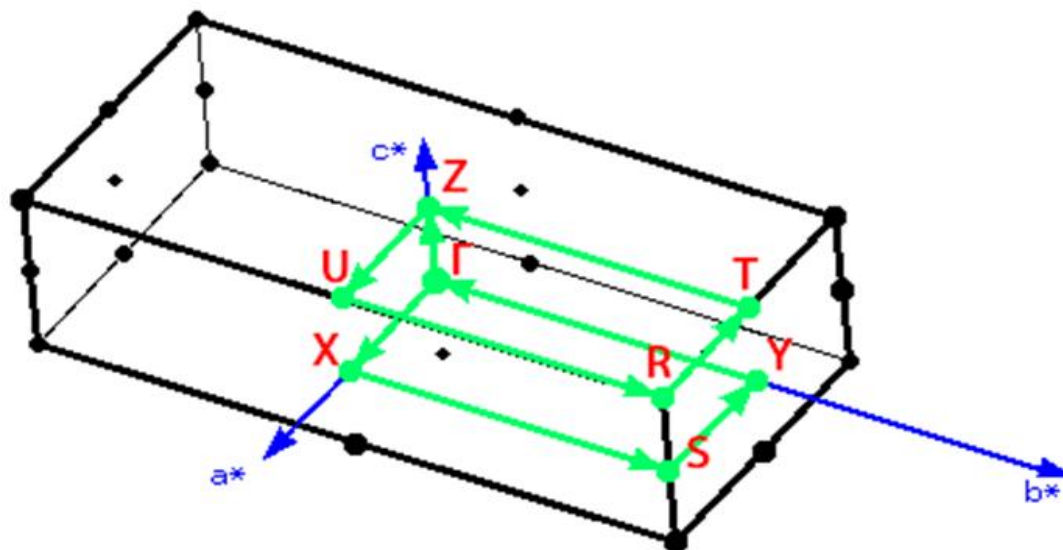


Fig. III.7: First brillouin zone of CaSiX_3 ($X = \text{S, Se, or Te}$) lattice with space group k-vector types.

The high-symmetry lines in [Fig. III.7](#) were used to calculate the electronic energy band structures of the compounds, but PBE-GGA method was not sufficiently accurate to produce high-precision results. Instead, we used the TB-mBJ approximation, proposed by Becke and Johnson [215] to improve upon the PBE-GGA results. [Fig. III.8](#), [III.9](#), and [III.10](#) illustrate the band structure results for CaSiS_3 , CaSiSe_3 , and CaSiTe_3 . The band gap values are shown in [Table III.6](#).

These diagrams show that there is only one compound, CaSiTe_3 in which the valence and conduction bands cross the Fermi level ([Fig. III.10](#)) exhibiting metallic behavior with $E_g = 0$ eV, regardless of whether the PBE-GGA or TB-mBJ method is used. To validate this result, we utilized the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional approximation [216], one of the hybrid functionals within density functional theory (DFT), using the QUANTUM ESPRESSO software [217]. The result indicated a band gap of 0.05 eV for CaSiTe_3 , which is notably minimal and is commonly found in materials such as semimetals, narrow-band gap semiconductors, and certain topological insulators. For instance, materials such as bismuth and graphite can show very small band gaps under particular conditions, although these gaps may close completely, leading to metallic behavior.

From [Fig. III.8](#), it appears that CaSiS_3 has a semiconducting behavior since the band gap value increased from 0.790 eV in the case of PBE-GGA to 3.020 eV in the case of TB-mBJ ([Table III.6](#)) with the same indirect band gap $[\Gamma-X]-[Y-\Gamma]$. This property is typical of wide band gap semiconductors, which are commonly used in high-power, high-frequency optoelectronic applications. As an example, previous studies on barium zirconium sulfide (BaZrS_3) and methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) have reported experimental band gaps of approximately 1.74 eV [17] and 1.58 eV [218], respectively, allowing for use in many applications, including photocatalysis and optoelectronic devices. Moreover, the successful synthesis of strontium zirconium sulfide (SrZrS_3) has been reported, exhibiting a band gap of 2.13 eV [92]. Additionally, CaSiS_3 shows the highest band gap value among the studied chalcogenide perovskites, and no higher or similar value was found.

[Fig. III.9](#) indicates that CaSiSe_3 , exhibits semiconducting behavior. The band gap value increases from 0.107 eV in PBE-GGA to 1.712 eV when using TB-mBJ ([Table III.6](#)), while maintaining the same indirect band gap $[\Gamma-X]-[T-Z]$. In comparison, BaZrS_3 possesses a direct band gap of 1.8 eV [219], which is approximately equal to the band gap of methylammonium lead

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iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) [218], one of the most commonly studied perovskites, particularly for solar cell applications.

It is clear from the study that replacing the chalcogen (X) atom in the compound's structure impacts not only its structural and mechanical properties but also its electronic behavior. The results demonstrate a notable decrease in bandgap energy from 3.020 eV in the presence of sulfur to 1.712 eV with selenium.

This change is due to differences in the electronic distribution of the substituted chalcogen atoms. The increase in electron density caused by atoms of different atomic radii, electronegativity values, and bonding characteristics, reduces the band gap energy. Remarkably, this decrease can lead to the complete disappearance of the band gap, as observed with the incorporation of tellurium (Te). This makes the compound ideal for applications requiring specific electronic properties, such as enhanced electrical conductivity or efficient light absorption in photovoltaic devices.

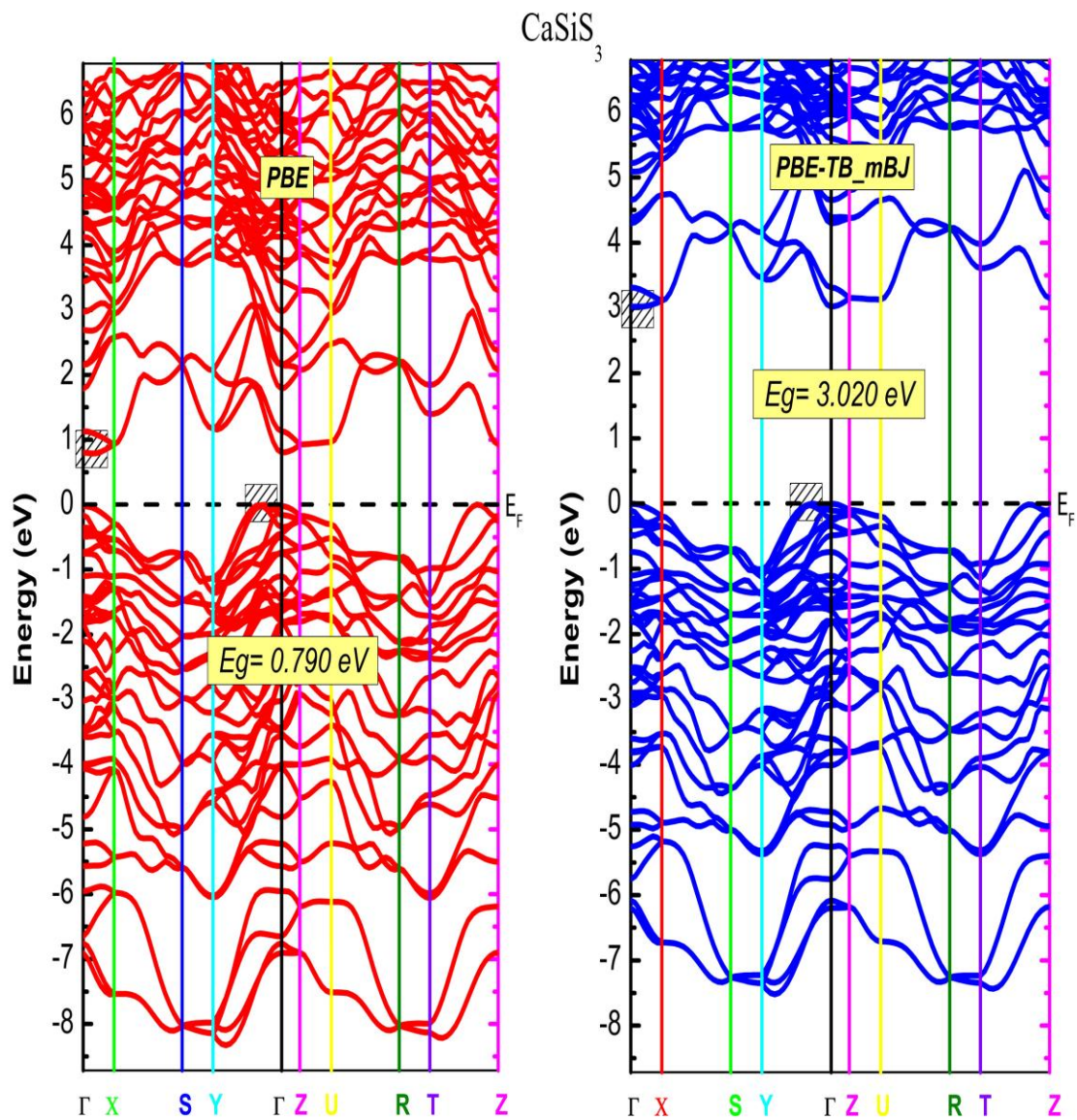


Fig. III.8 The calculated band structure for CaSiS_3 using the PBE-GGA and TB-mBJ approach.

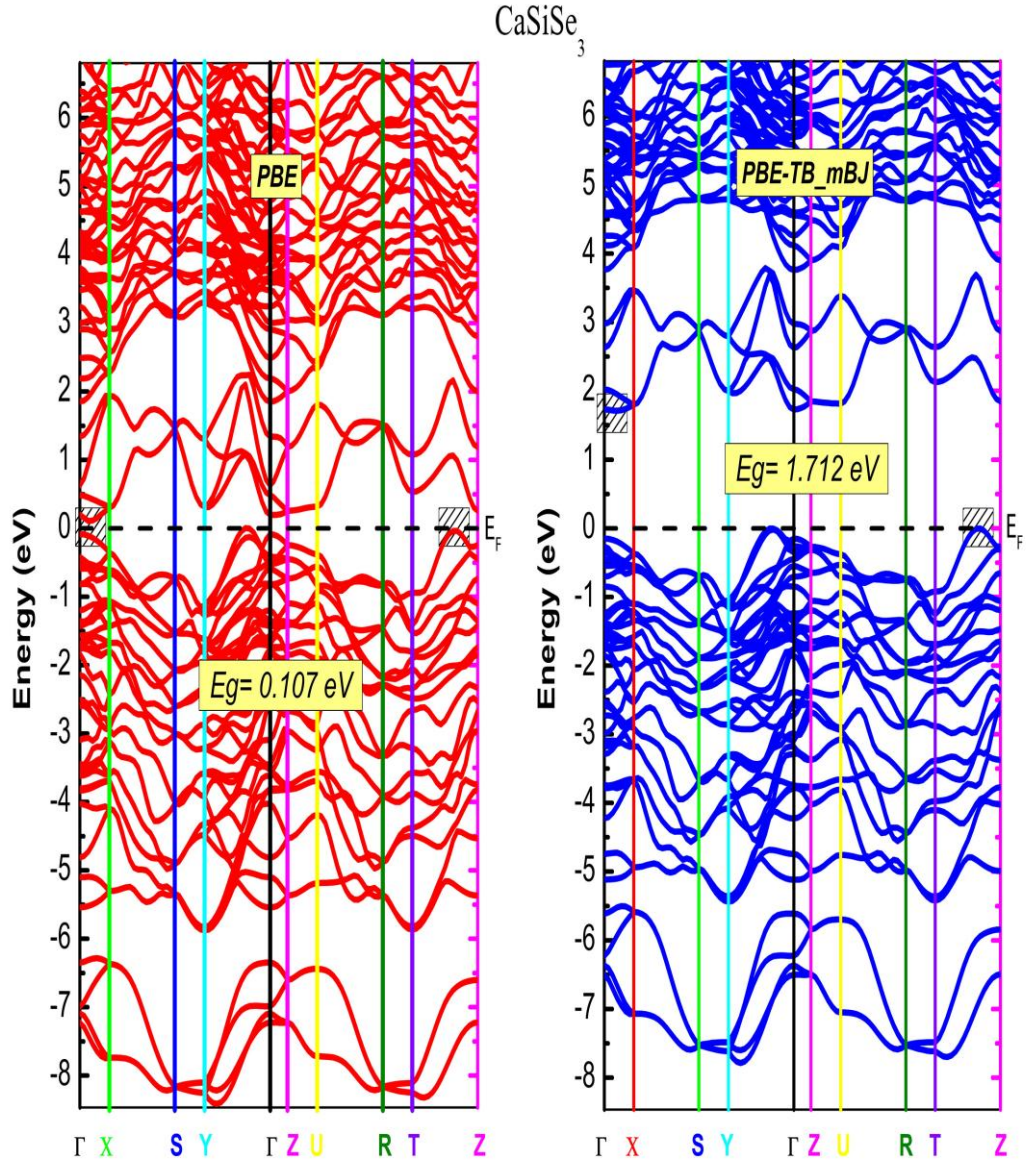


Fig. III.9: The calculated band structure for CaSiSe₃ using the PBE-GGA and TB-mBJ approach.

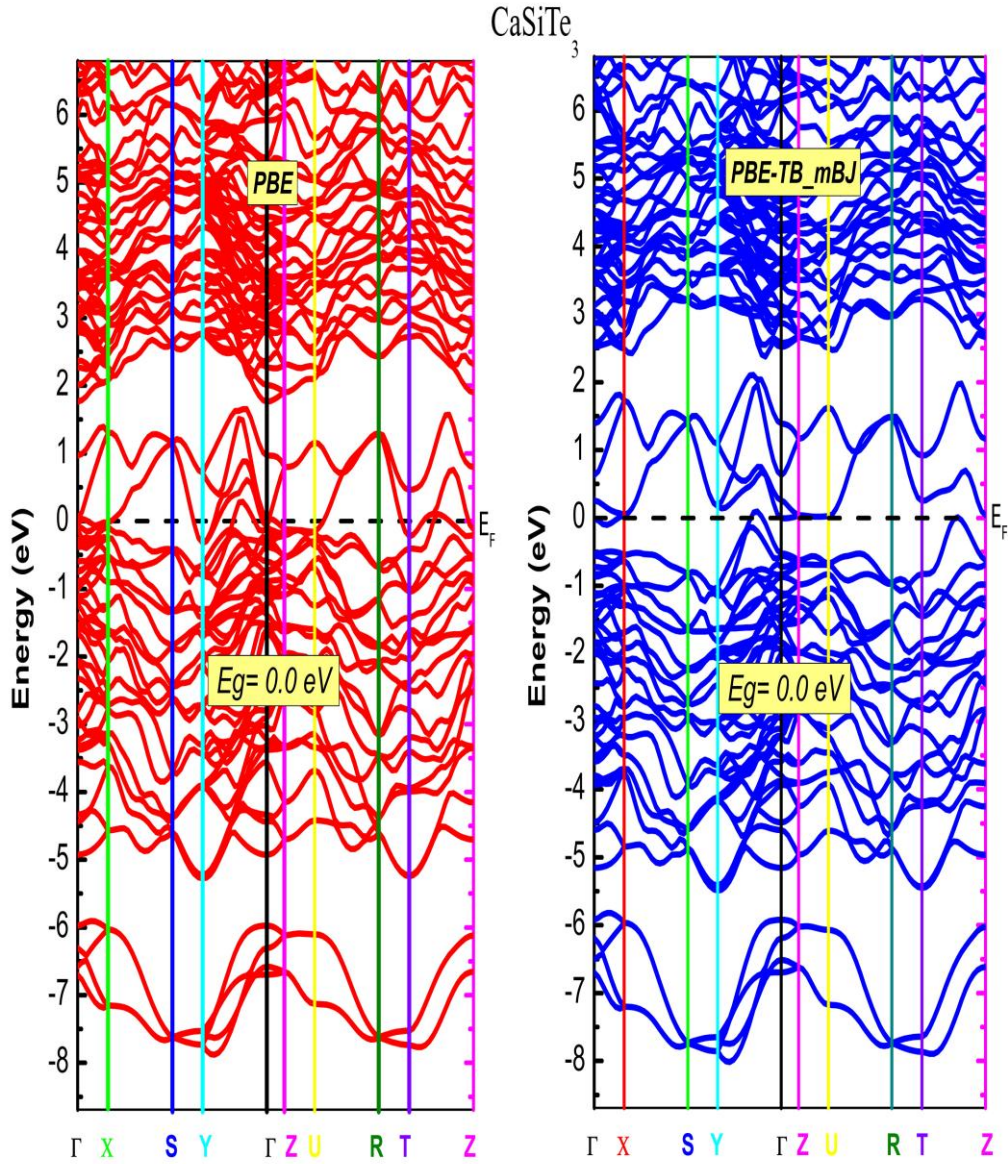


Fig. III.10: The calculated band structure for CaSiTe_3 using the PBE-GGA and TB-mBJ approach.

Table III.6: Band gap (E_g) values of chalcogenide perovskite CaSiX_3 ($\text{X}=\text{S}$, Se , and Te) compounds were estimated using both PBE-GGA and TB-mBJ approach.

	Nature	Direction	Band-gap energy (eV)		
			PBE-GGA	TB-mBJ	HSE ₀₆
CaSiS₃	Indirect	$[\Gamma\text{-X}]$ - $[\text{Y-}\Gamma]$	0.790	3.020	--
CaSiSe₃	Indirect	$[\Gamma\text{-X}]$ - $[\text{T-Z}]$	0.107	1.712	--
CaSiTe₃	--	--	0.0	0.0	0.05

III.5.3.2. Density of States

One significant and fascinating electronic characteristic in solid-state physics is the density of states (DOS). It is useful for examining the composition of electronic bands. The DOS allows us to identify the key characteristics of each energy region, as well as the nature of bonds and the states that contribute to them. We can also precisely determine the band gap energy using DOS data.

Figures (III.11, III.12, and III.13) show the projected density of states (TDOS and PDOS) of CaSiS_3 , CaSiSe_3 , and CaSiTe_3 calculated using the modified Becke Johnson functional of Tran and Blaha (TB-mBJ), to better understand the band structure especially the characteristics near the valence band maximum (VBM) and conduction band minimum (CBM). The vertical line represents the Fermi level (0 eV). The density of states (DOS) depicted in the figures correlates with and validates the relationship between material properties as indicated by the band structure. In particular, the DOS exhibits the same behavior as that observed in the band structure.

Understanding the details of specific contributions of various atomic states can be further assisted by analyzing the partial density of states (PDOS) [220]. we discuss the density of the states in the energy range from -8.5 eV to 6.5 eV. We plotted the widened outlook of the DOS at the

Chapter III: Physical properties: calculation, results, and discussion

Fermi level. Furthermore, we can observe that the VBM values of the DOS near the Fermi level for CaSiS_3 and CaSiSe_3 ([Fig. III.11](#) and [III.12](#)) are nearly zero.

The DOS is primarily divided into four parts: the conduction band (CB), the upper valence band (VB_{High}), and lower valence band (VB_{Low}). For the three materials. the DOS of the lower part of the valence energy region ($\sim -7.57 < \text{VB}_{\text{Low}} < -6.05$ eV for CaSiS_3 , and $\sim -7.87 < \text{VB}_{\text{Low}} < -5.47$ eV of CaSiSe_3) is associated with the PDOS of Si_3s states for both compounds, along with contribution of S_3p, and Se_4p states, respectively.

In contrast, the upper part of the valence band ($\text{VB}_{\text{Low}} < \text{VB}_{\text{High}} < 0$ eV) is associated with the Si_3p states for both compounds, together with S_3p (CaSiS_3), and Se_4p (CaSiSe_3) states. conduction band (> 2.96 eV for CaSiS_3 , and > 1.63 eV of CaSiSe_3) is associated with the PDOS contributions from the same states that constitute the $\text{VB}_{\text{High}} + \text{VB}_{\text{Low}}$ for each compound. We notice that the Te_5p and Si_3s/3p states attributed to both valance and conduction regions in CaSiTe_3 .

The density of states (Te_5p) crosses the Fermi level, confirming the validity of the metallic bonding type observed in the CaSiTe_3 compound, as supported by Poisson's ratio obtained from study of its elastic properties.

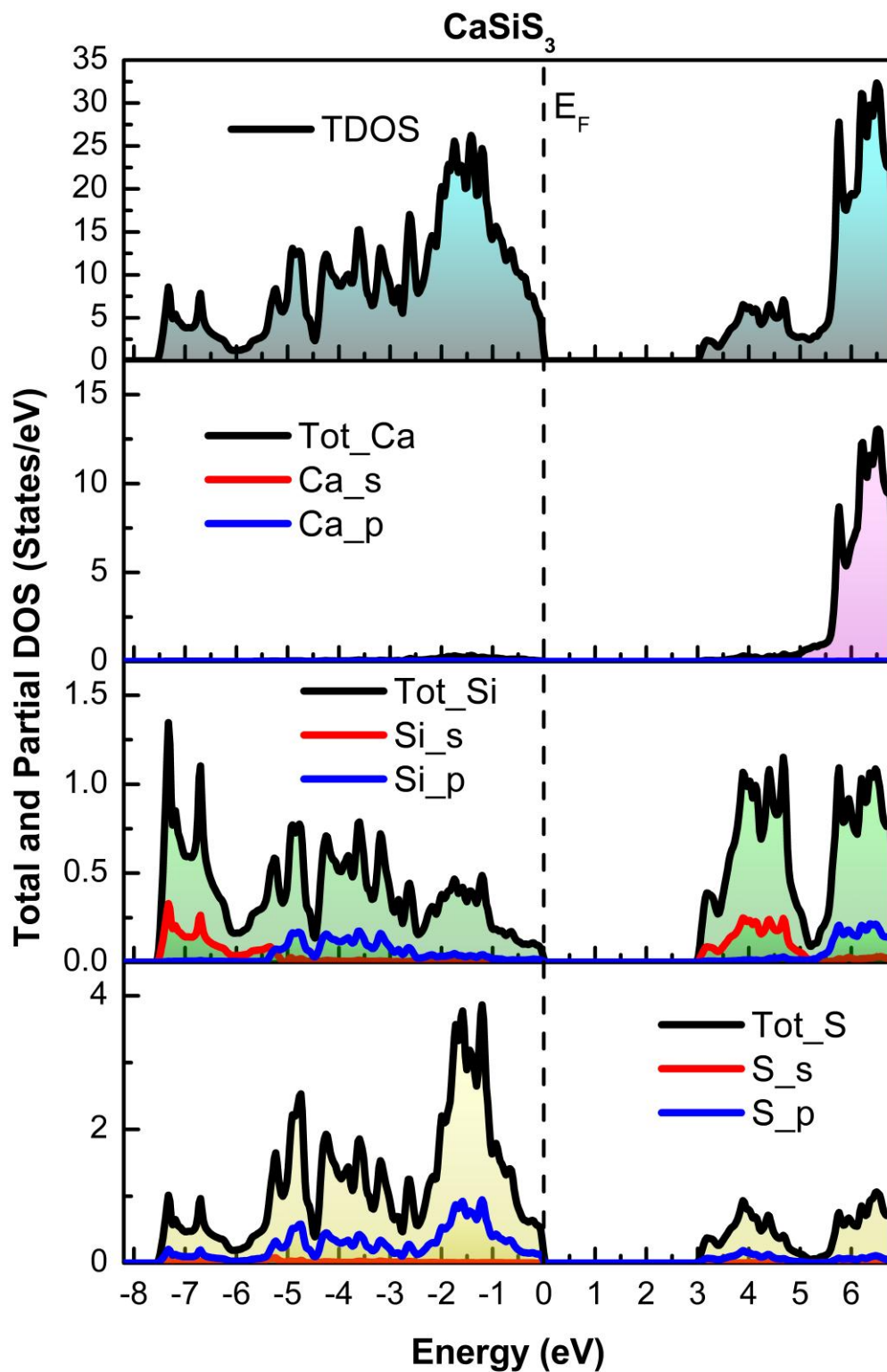


Fig. III.11: The calculated TDOS and PDOS of CaSiS₃ using the TB-mBJ.

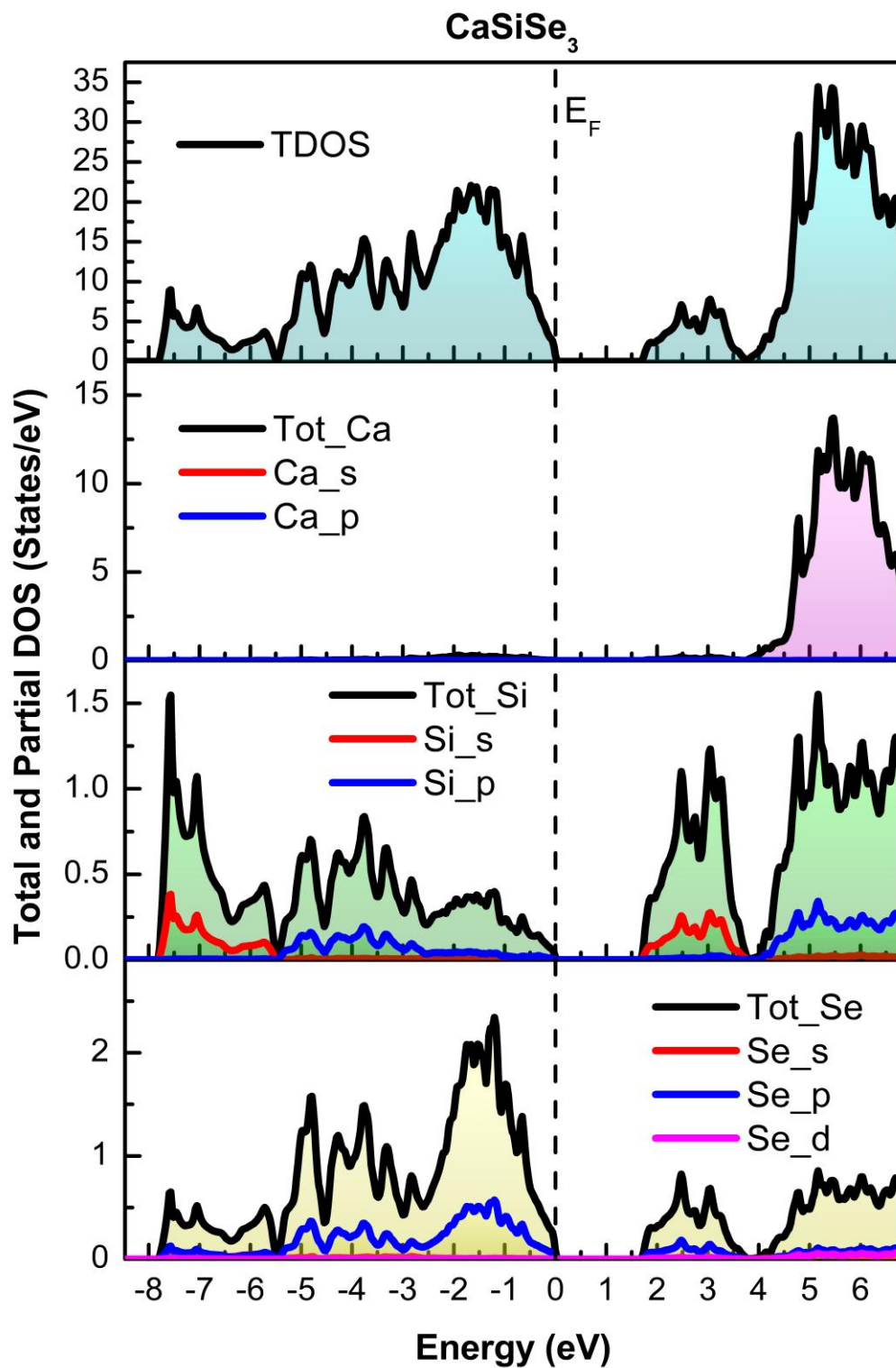


Fig. III.12: The calculated TDOS and PDOS of CaSiSe₃ using the TB-mBJ.

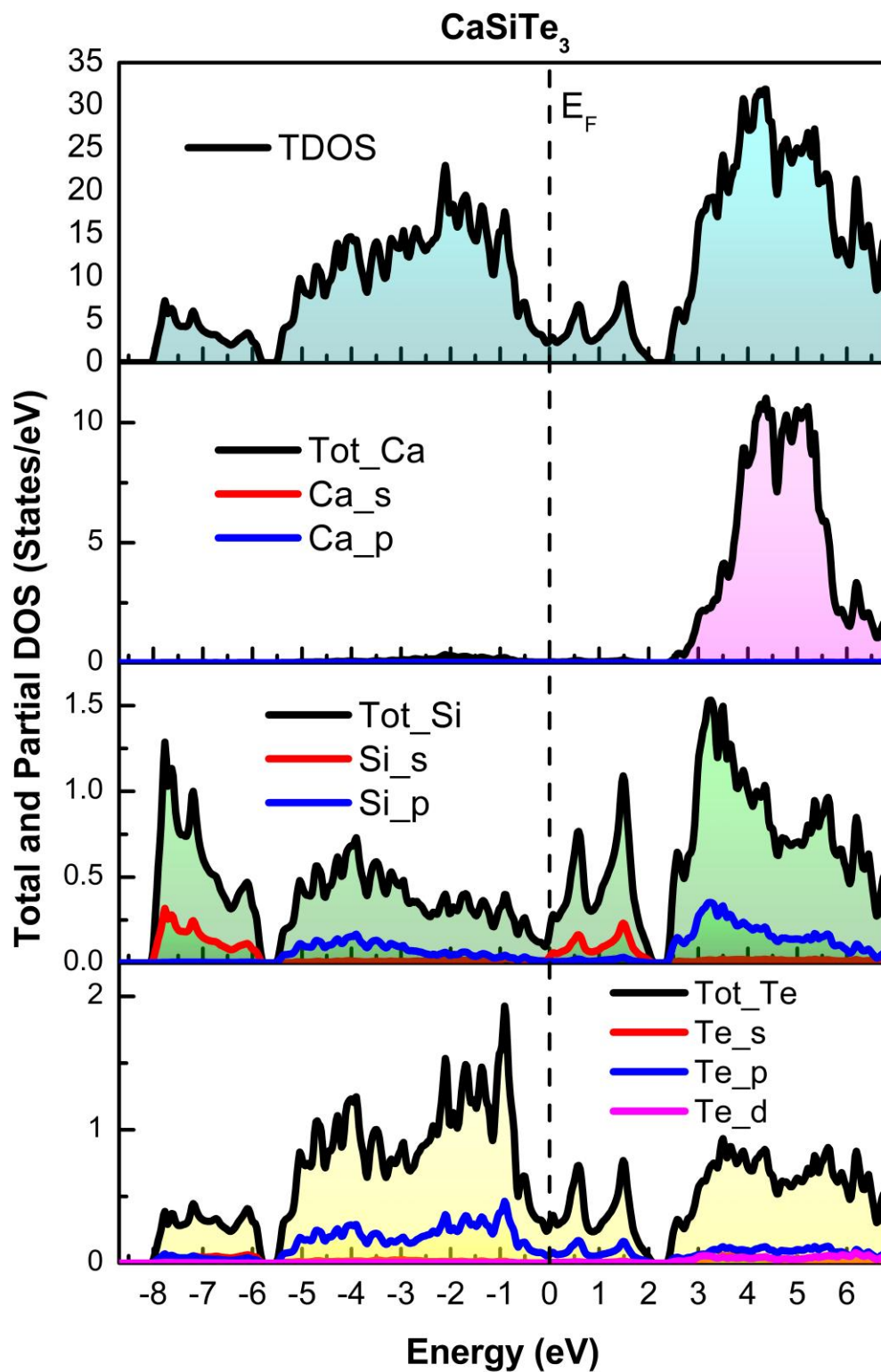


Fig. III.13: The calculated TDOS and PDOS of CaSiTe₃ using the TB-mBJ.

III.5.4. Optical Properties

In addition to this theoretical study on the geometrical, elastic, and electronic properties of CaSiX_3 ($X = \text{S}$ and Se), we have also analyzed various optical property parameters, such as the complex dielectric function, the absorption coefficient $\alpha(\omega)$, and reflectivity $R(\omega)$, and the refractive index $n(\omega)$ [221–224], which are essential to investigating their responses to the incident photons for possible applications in optoelectronic devices.

We understand that a material's optical properties are strongly dependent on its electronic properties. When a material is exposed to light with sufficient energy, electrons are excited from states below the Fermi level (E_F) to states above it. Understanding the behavior of materials under light irradiation requires studying all parameters related to optical properties.

III.5.4.1. Dielectric Function

The complex dielectric function describes the response of electrons in a substance [225–227], which is defined as $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. Here, the complex dielectric wave function's real and imaginary components are indicated by the symbols $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, respectively. Concerning the real part $\varepsilon_1(\omega)$, which describes the medium's response under an external electric field, it can be derived using the Kramers-Kronig relations [207,228]. The imaginary part $\varepsilon_2(\omega)$ illustrates the transition from the occupied states to vacant states as light traverses the medium [207,228,229]. We can compute the remaining parameters using the $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, which can be derived using the following equations [228]:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (\text{III.26})$$

$$\varepsilon_2(\omega) = \frac{Ve^2}{2\pi\hbar m^2 \omega^2} \int d^3k \sum_{mn} \left| \langle kn | p | kn' \rangle \right|^2 f(kn) \times (1 - f(kn')) \delta(E_{kn} - E_{kn'} - \hbar\omega) \quad (\text{III.27})$$

The dielectric function $\varepsilon(\omega)$ is used to understand the interaction between materials and electromagnetic waves. **Fig. III.14 (a, b)** displays the values of $\varepsilon_1(\omega)$. At an energy of $\omega = 0$ eV, the dielectric constant $\varepsilon_1(0)$ in the $\langle XX \rangle$, $\langle YY \rangle$ and $\langle ZZ \rangle$ directions for CaSiS_3 are 4.76, 4.82, and 4.52, and for CaSiSe_3 are 6.30, 6.32, and 5.68 (see **Table III.7**). In both materials, we can arrange the high-value direction as follows $\varepsilon_1(\omega)_{xx} > \varepsilon_1(\omega)_{yy} > \varepsilon_1(\omega)_{zz}$, as shown in **Table III.8**. For CaSiS_3 , the highest value is 14.97 compared to 14.46 for CaSiSe_3 along the $\langle XX \rangle$ direction.

CaSiSe₃ exhibits the greatest values for the $\langle XX \rangle$ and $\langle ZZ \rangle$ directions (10.58 and 12.36, respectively), whereas CaSiS₃ displays the lowest values (9.79 and 10.48, respectively).

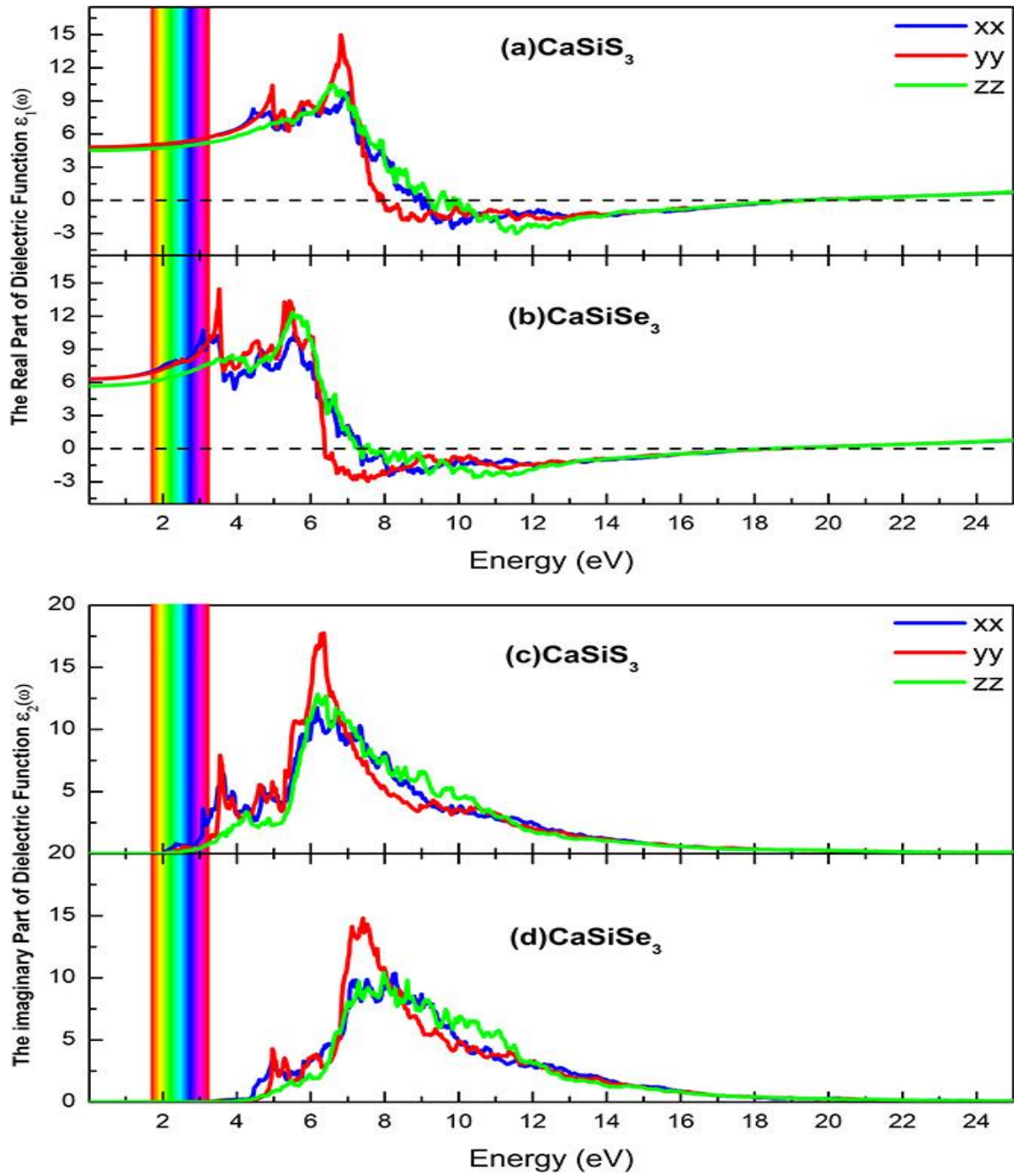


Fig. III.14: The real and imaginary parts of the dielectric function for CaSiS₃ and CaSiSe₃.

The electronic properties displayed semiconducting behavior, that was consistent with the optical absorption onsets in $\varepsilon_2(\omega)$ spectra illustrated in [Fig. III.14 \(d, e\)](#). Furthermore, the first peak that is maximal in the imaginary part is known as the first absorption peak [230]. Along the three directions $\langle XX \rangle$, $\langle YY \rangle$ and $\langle ZZ \rangle$, the values for CaSiSe_3 are 3.57 at 4.97 eV, 4.28 at 4.97 eV, and 2.24 at 5.97 eV, respectively, while for CaSiS_3 they are 6.47 at 3.63 eV, 7.91 at 3.55 eV, and 3.37 at 4.26 eV, respectively. It is noteworthy that CaSiSe_3 exhibits higher peaks in the $\langle YY \rangle$ direction, with a value of 17.77 at 6.35 eV, whereas CaSiS_3 shows 14.80 at 7.42 eV, both exceeding the values in the $\langle XX \rangle$ $\langle ZZ \rangle$ direction, as shown in [Table III.8](#).

III.5.4.2. Absorption Coefficient

When subjected to an external electric field, the real part of the dielectric constant induces polarization in the material and governs its ability to absorb light. This behavior is described by the following equation [230]:

$$\alpha(\omega) = 2\omega \left[\frac{(\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega))^{1/2} - \varepsilon_1(\omega)}{2} \right]^{1/2} \quad (\text{III.28})$$

This photon absorption triggers interband and intraband transitions, generally classified into direct and indirect band transitions. We can see that there are two ranges where absorption occurs in the two compounds; from 0 to 25 eV and from 25 to 35 eV, as shown in [Fig. III.15 \(a, b\)](#). For CaSiS_3 , the absorption coefficient rises steeply from 3.01 eV, as seen in [Fig. III.15 \(a\)](#). The highest value (see [Table III.8](#)) corresponds to α_{zz} , about $2.37 \times 10^6/\text{cm}$ around 11.52 eV, where the α_{xx} and α_{yy} are $2.09 \times 10^6/\text{cm}$ at 9.81 eV, and $1.99 \times 10^6/\text{cm}$ at 11.55 eV, respectively.

Likewise, as seen in [Fig. III.15 \(b\)](#) CaSiSe_3 exhibits an upward trend from 1.85 eV, with a slightly lower peak absorption coefficient α_{zz} of approximately $2.06 \times 10^6/\text{cm}$ at the energy level 10.41 eV, where the α_{yy} gives the value of $1.88 \times 10^6/\text{cm}$ at 6.38 eV and α_{xx} reaches $1.84 \times 10^6/\text{cm}$ at 8.10 eV, respectively.

The absorption range of 27–550 nm primarily includes the ultraviolet (UV) region and a small segment of the visible spectrum. This strong absorption of high-energy photons suggests that CaSiS_3 compound is well-suited for UV photodetectors and optoelectronic applications. In contrast, CaSiSe_3 exhibits absorption extending into the visible red and near-infrared regions,

which is advantageous for photovoltaic and tandem solar cell applications. These optical properties underscore the potential of both materials for use in next-generation optoelectronic devices.

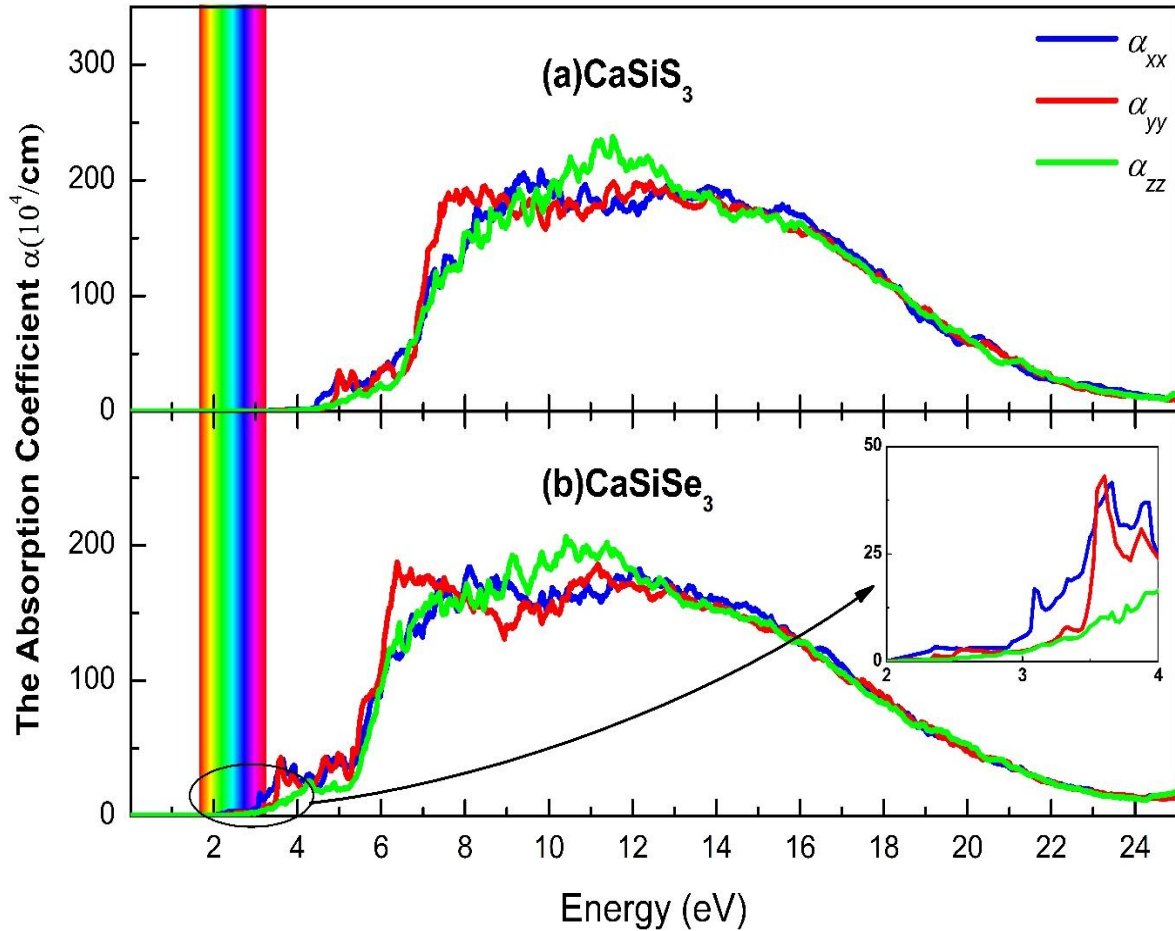


Fig. III.15: The absorption coefficient for CaSiS_3 and CaSiSe_3 .

III.5.4.3. The Reflectivity and Refractive index.

Reflectivity $R(\omega)$ indicates the quantity of light reflected within the medium [226]. We calculated $R(\omega)$ for CaSiS_3 and CaSiSe_3 in their orthorhombic phases, as illustrated in **Fig. III.16 (a-b)**. At an energy of $\omega = 0$ eV, the reflectivity $R(0)$ in the $\langle XX \rangle$, $\langle YY \rangle$ and $\langle ZZ \rangle$ directions for CaSiS_3 measures 0.134, 0.14, and 0.13, respectively, while for CaSiSe_3 , are 0.19, 0.19, and 0.17 in the same directions (**Table III.7**).

Fig. III.16 (a-b) shows that the materials under study are semiconductors, since the reflectivity values are minimal in all directions of the absorption spectrum ($\langle XX \rangle$, $\langle YY \rangle$, and $\langle ZZ \rangle$). The

highest reflectivity value was at R_{ZZ} , reaching 0.51 (X= S) and 0.52 (X= Se). Reflectivity is significantly lower in the UV region, which enhances absorption in this area. After the energy gap value, the reflection of photons, if any, is nearly non-existent, confirming that these materials are highly suitable for solar cell applications.

In **Fig. III.16 (a-b)**, we illustrate the spectral changes in the refractive index $n(\omega)$ for CaSiX_3 (X= S and Se) as determined using the TB-mBJ method. The refractive index of semiconductor materials plays a significant role in their transparency to incoming photons [231]. It is closely related to the imaginary part of the dielectric function $\varepsilon_2(\omega)$ since the exact same graph shape appears with different values. **Table III.7** shows the values of the $n(0)$, the and $n(\omega)$ values for the two compounds reach a maximum value within the 3.4–8 eV range, and subsequently decrease at higher energies. The dispersion curves of n and k for CaSiS_3 reach their high peak with the <YY> direction around 6.81 eV and 7.61 eV, respectively, and for CaSiSe_3 around 5.51 eV and 6.38 eV, respectively. The reflectivity $R(\omega)$ and refractive index $n(\omega)$, it can be derived using:

$$R(\omega) = \left[\frac{\sqrt{\varepsilon_1(\omega) + i\varepsilon_2(\omega)} - 1}{\sqrt{\varepsilon_1(\omega) + i\varepsilon_2(\omega)} + 1} - \varepsilon_1(\omega) \right]^2 \quad (\text{III.29})$$

$$n(\omega) = \left[\frac{\varepsilon_1(\omega)}{2} + \frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}}{2} \right]^{\frac{1}{2}} \quad (\text{III.30})$$

Table III.7: The optical dielectric constants, static reflectivity, and refractive index of CaSiX_3 (X=S and Se) chalcogenide.

	$\varepsilon_I(0)$			$R(0)$			$n(0)$		
	XX	YY	ZZ	XX	YY	ZZ	XX	YY	ZZ
CaSiS_3	4.76	4.82	4.52	0.14	0.14	0.13	2.18	2.20	2.13
CaSiSe_3	6.30	6.32	5.68	0.19	0.19	0.17	2.51	2.51	2.38

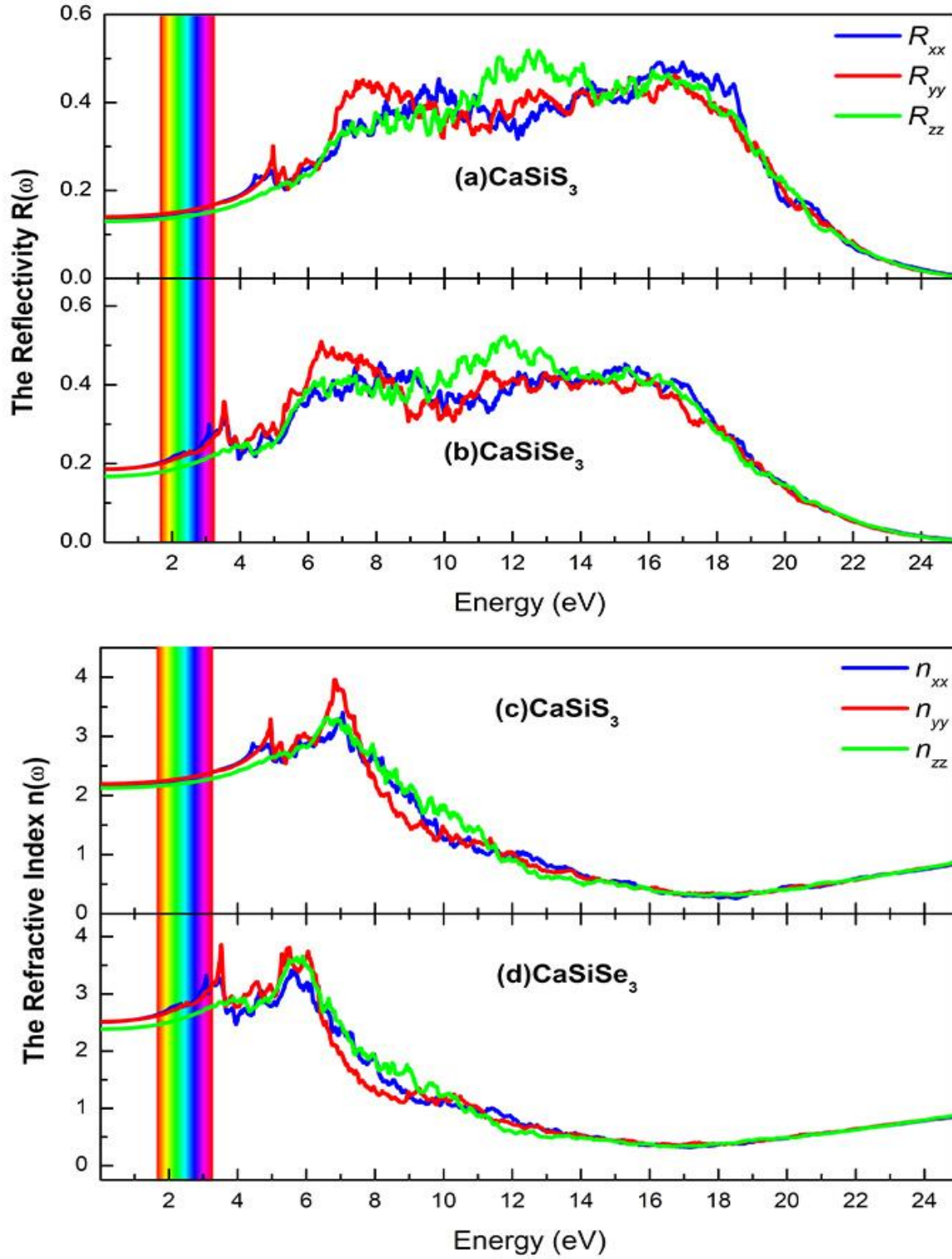


Fig. III.16: The calculated reflectivity $R(\omega)$ (a-c) and the refractive index $n(\omega)$ using the TB-mBJ for CaSiX_3 ($X = \text{S}$ and Se).

Table III.8: The higher values for the real and imaginary part of dielectric function, the absorption coefficient, and the reflectivity.

		CaSiS ₃	CaSiSe ₃
$\varepsilon_1(\omega)$	XX	9.79 at 7.06 eV	10.58 at 5.56 eV
	YY	14.97 at 6.82 eV	14.46 at 3.52 eV
	ZZ	10.48 at 6.60 eV	12.36 at 5.51 eV
$\varepsilon_2(\omega)$	XX	10.36 at 8.29 eV	11.75 at 6.16 eV
	YY	14.80 at 7.42 eV	17.77 at 6.35 eV
	ZZ	10.40 at 7.99 eV	12.83 at 6.19 eV
$\alpha(\omega)$	XX	$2.09 \times 10^6/\text{cm}$ at 9.81 eV	$1.84 \times 10^6/\text{cm}$ at 8.10 eV
	YY	$1.99 \times 10^6/\text{cm}$ at 11.55 eV	$1.88 \times 10^6/\text{cm}$ at 6.38 eV
	ZZ	$2.37 \times 10^6/\text{cm}$ at 11.52 eV	$2.06 \times 10^6/\text{cm}$ at 10.41 eV
$R(\omega)$	XX	0.49 at 16.99 eV	0.45 at 8.12 eV
	YY	0.46 at 16.78 eV	0.51 at 6.38 eV
	ZZ	0.52 at 12.45 eV	0.52 at 11.76 eV

III.5.5. Thermoelectric properties

To better understand these substances, we study the thermal properties, that are crucial for future uses, and this is done using the BoltzTraP2 code, with the use of Fermi energy treated as the zero-temperature chemical potential [232]. Since the materials show semiconductor behavior, they possess many free electrons that contribute to electrical conductivity by crossing the band gap between the valence and conduction bands during excitation.

Utilizing semi-classical Boltzmann transport equations, we examined the Seebeck coefficient (S), electrical conductivity (σ/τ), and electronic thermal conductivity (κ_e/τ) at temperatures of 300K, 500K, and 700K using the BoltzTrap2 code [233]. The unit-cell volume, Fermi-Dirac distribution function, and chemical potential are denoted by Ω , f , and μ , respectively.

$$\sigma_{\alpha\beta}(T, \mu) = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\varepsilon) \left[-\partial f_{\mu}(T, \varepsilon) \right] d\varepsilon \quad (III.31)$$

$$\kappa_{\alpha\beta}(T, \mu) = \frac{1}{e^2 T \Omega} \int \sigma_{\alpha\beta} \varepsilon (\varepsilon - \mu)^2 \frac{\partial f_{\mu}(T, \varepsilon)}{d\varepsilon} \quad (III.32)$$

$$S = \frac{e}{T \sigma} \int \sigma_{\alpha\beta}(\varepsilon) (\varepsilon - \mu) \left[\frac{-\partial f_{\mu}(T, \varepsilon)}{\partial \varepsilon} \right] \quad (III.33)$$

The main topic of this section is the analysis of suitable data for the Seebeck coefficient. Determining this coefficient necessitates the combination of accurate electrical and thermal measurements, as the Seebeck coefficient is the ratio of the potential difference (μ) that results from a temperature difference T [234,235].

In **Fig. III.17 (a, b)**, the Seebeck coefficient versus chemical potential depicted at different temperatures shows that it remains stable for CaSiS_3 , suggesting that the material has a robust thermoelectric property across a wide temperature range. In contrast, CaSiSe_3 exhibits a decrease in the saw tooth profile with the increasing temperature, and both compounds show the same transition from the p-type (positive zone) to the n-type (negative zone). The Seebeck coefficient values are 1.52 mV/K at 300, 500, 700, and 900 K for CaSiS_3 , and 1.52 mV/K at 300 K, 1.51 mV/K at 500 K, 1.14 mV/K at 700 K, and 0.90 mV/K at 900 K for CaSiSe_3 .

The electrical conductivity (σ/τ) diagram, which represents the materials ability to conduct electric current, diagram that it shifts shows that it shifts from the p-region with low conductivity to the n-region with high conductivity, with conductivity decreasing as the temperature increases. These measurements reflect the behavior and distribution of charge carriers.

The highest values are detected at room temperature, and the replacement of the S atom with Se results in a small decrease in conductivity in the n-type region, from 1.86 to $1.67 \times 10^{20} (\Omega\text{ms})^{-1}$, while the p-type region remains unchanged at $1.48 \times 10^{20} (\Omega\text{ms})^{-1}$ for both compounds. It is worth noting that the thermal conductivity is suppressed in two energy ranges: from -1.29 to 1.52 eV for CaSiS_3 , and from -0.64 to 0.72 eV for CaSiSe_3 , because the movement of electrons within charge carriers is very limited. These suppressed regions correspond to the energy ranges where the Seebeck coefficient is high.

The electronic thermal conductivity divided by the relaxation time (k_e/τ) for CaSiS_3 and CaSiSe_3 is depicted in **Fig. III.17 (e, f)**. Both compounds exhibit the same behavior, the thermal

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conductivity increasing as the temperature rises, in accordance with the Wiedemann's-Franz law. As observed, the values show an upward trend as the chemical potential deviates from the Fermi level ($\mu = 0$). This increase is also evident with the rise in temperature starting from 300 K. The correlation between the varying chemical potential and temperature highlights the sensitivity of k_e/τ to these parameters.

The largest peak at 900 K has a value of 2.49×10^{14} (W/m.k.s) at -4.79 eV in the p-type region and 3.37×10^{14} (W/m.k.s) at 5.10 eV in-type region for CaSiS_3 , and for CaSiSe_3 of 2.72×10^{14} (W/m.k.s) at the chemical potential of -4.42 eV at the p-type region and 3.29×10^{14} (W/m.k.s) at 4.65 eV in the p-type region. The limited (Ke/τ) values, particularly noticeable at room temperature, suggest minimal electronic contributions to thermal conductivity, making these compounds especially advantageous for thermoelectric applications [236].

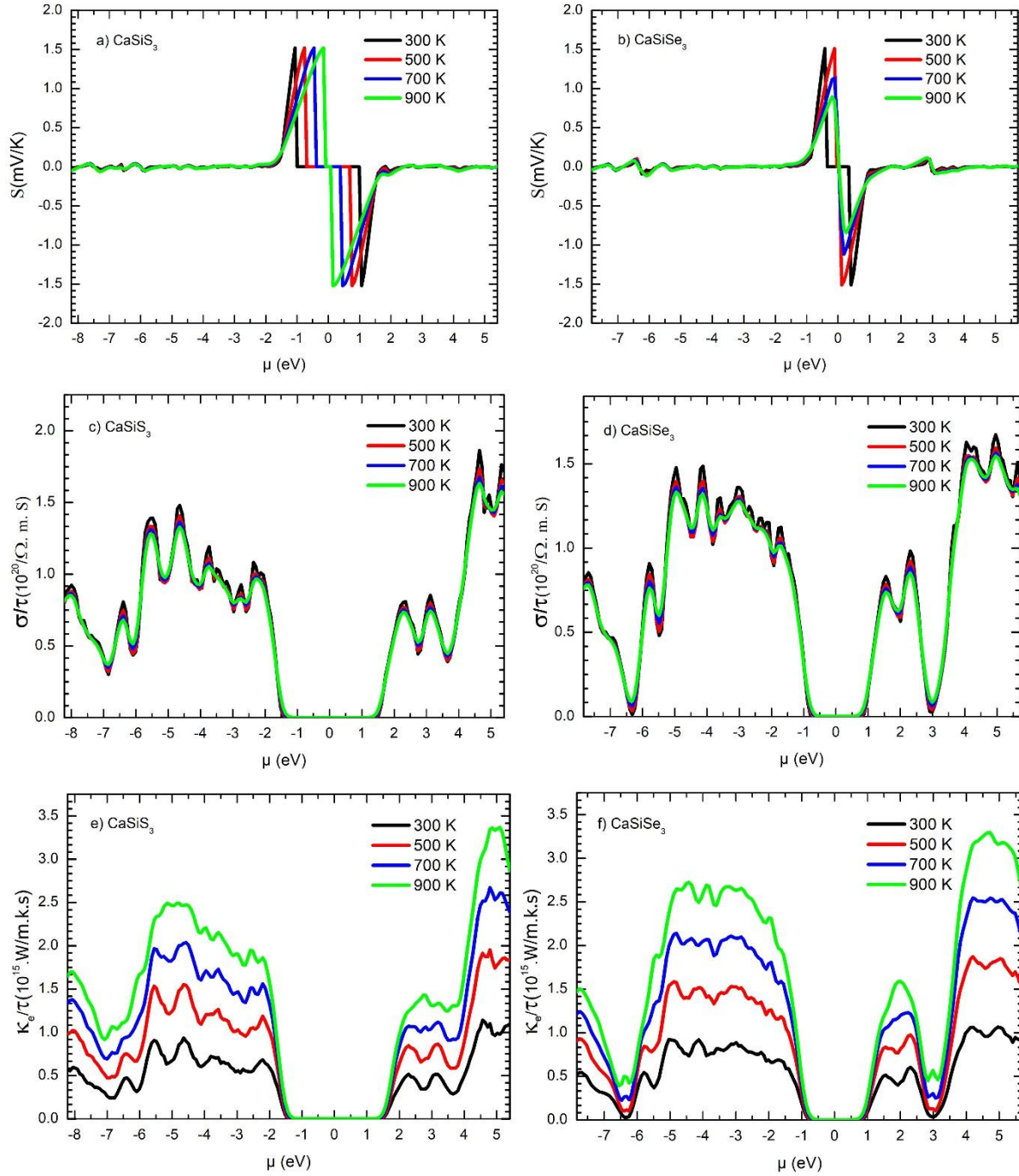


Fig. III.17: Seebeck coefficient (a-b), electrical conductivity (c-d), electronic part of the thermal conductivity (e-f), of CaSiS₃ and CaSiSe₃.

Using the figure of merit (ZT) shown in [Fig. III.18](#), the thermoelectric characteristics of these materials in their orthorhombic configuration were assessed across the temperature range of

300–900 K. With a ZT value of 0.18 at room temperature (300 K), CaSiSe₃ demonstrate a remarkable thermoelectric efficiency, performing better than CaSiS₃, which has a ZT of 0.06. These materials are appropriate for a range of thermoelectric applications, since the ZT value peaks at 0.47 for CaSiS₃ at 900 K and 0.40 for CaSiSe₃ at 550, highlighting their capacity to sustain positive thermoelectric performance even at high temperatures.

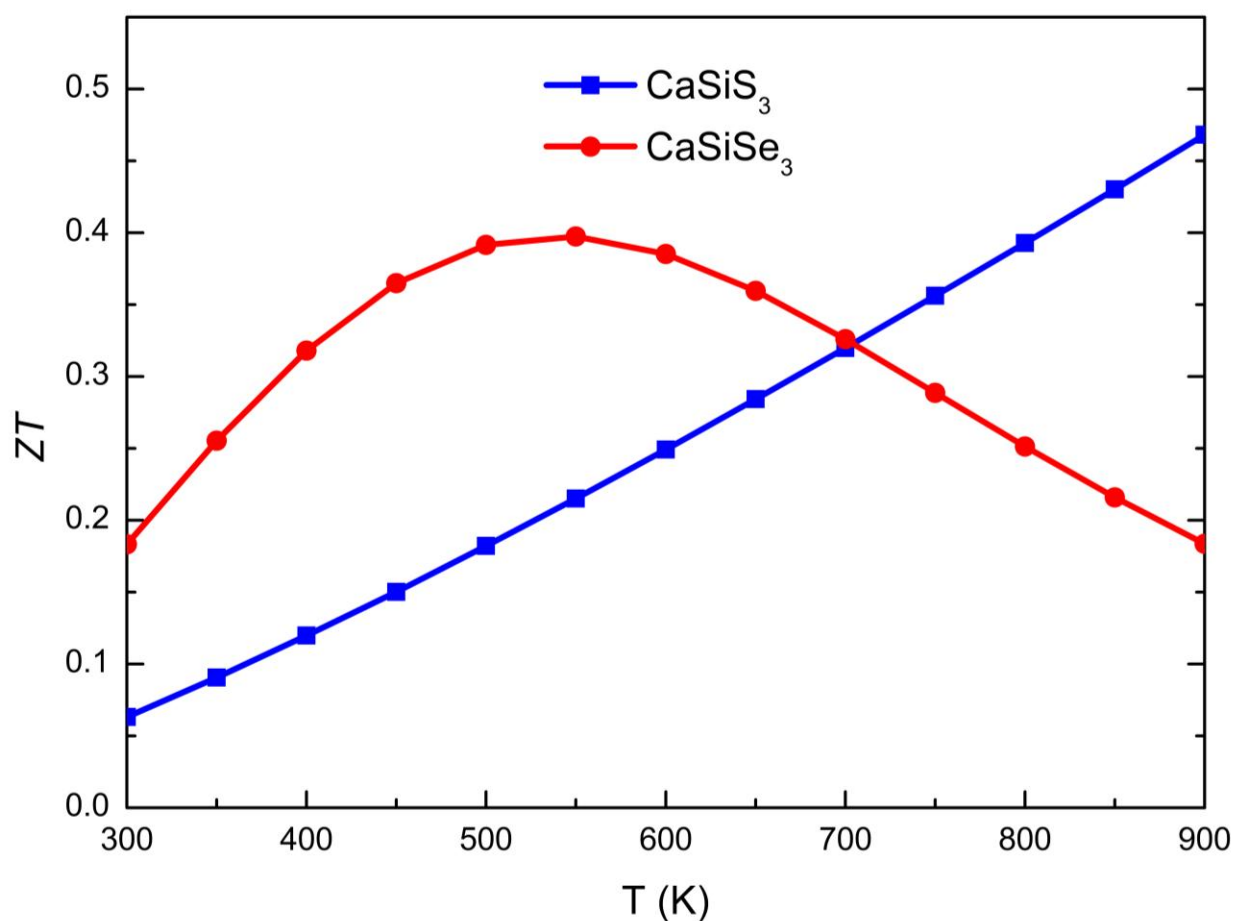


Fig. III.18. Profile of ZT-merit for CaSiX₃ (X= S or Se).

Fig. III.19 displays the power factors for all materials. This graphic demonstrates how temperature influences the partial efficiency of a thermoelectric device when using chemicals that have yet to be fully characterized. This material is a promising candidate for renewable energy applications in thermoelectric systems because of its exceptional thermoelectric performance of $30.56 \times 10^{10} (W^I, K^2, s^{-I})$ at 900K for CaSiS₃ and $10.50 \times 10^{10} (W^I, K^2, s^{-I})$ for CaSiSe₃.

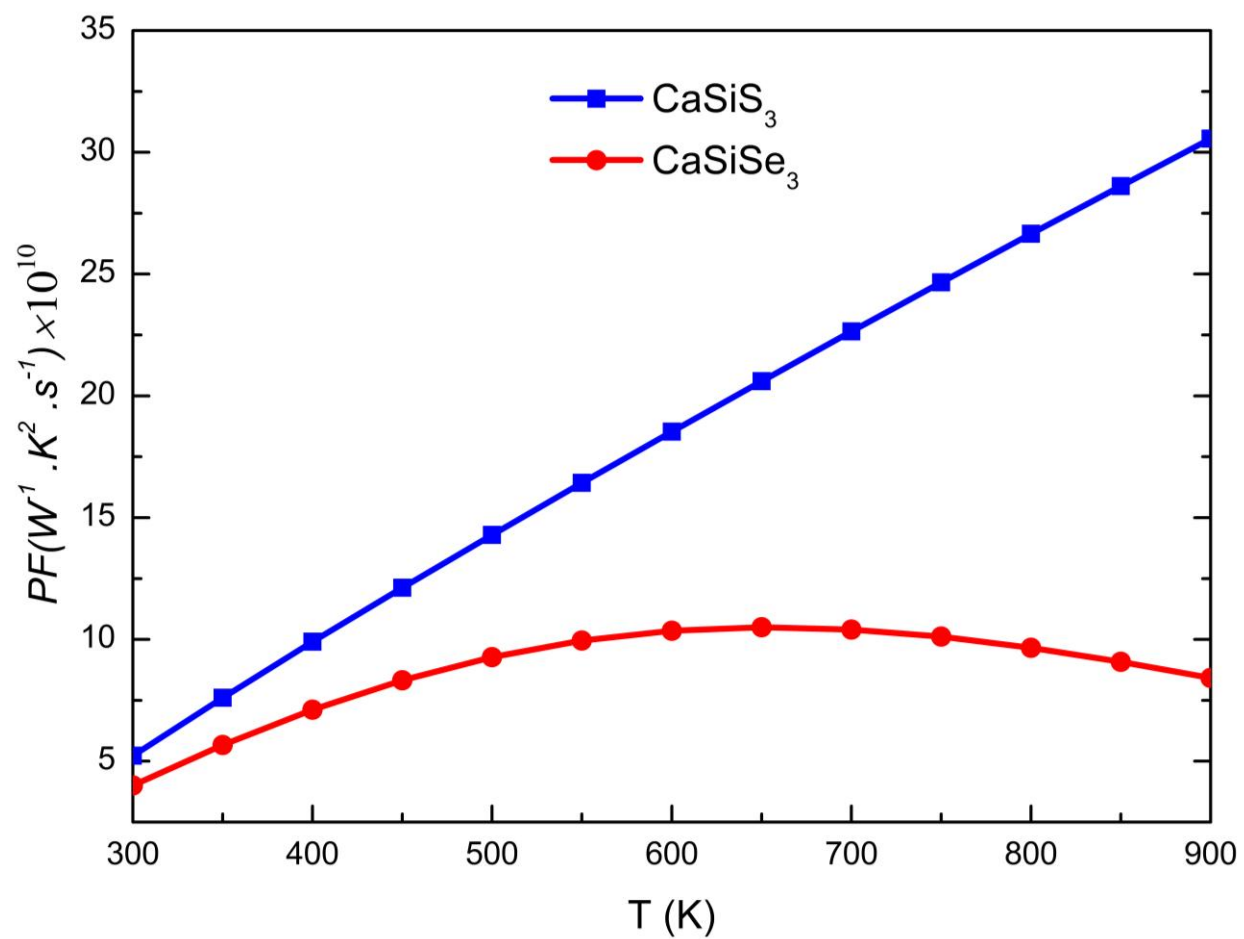


Fig. III.19. Profile of power factor for CaSiX_3 (X= S or Se).

***Chapter IV: Solar cell
application within the studied
materials by using (AMPS-
1D)***

IV.1. Introduction

The efficiency and quality of materials have become the main objectives for both manufacturers and users in thin-film solar cell manufacturing processes. Understanding and setting up the parameters related to various features of solar cells is crucial prior to manufacture. We can facilitate this process by running simulations using several programs. In this chapter, we present a simulation study of two types of perovskite chalcogenide solar cells using WxAMPS-1D [237].

It is worth noting that these two structures of solar cells under study are part of a multilayer thin-film system. Studying the effect of optical and electrical parameters on the cells is important. Our main goal was to examine the simulation findings of two distinct solar cell system. First, the simulation software and cell structure were presented based on the fundamental parameters being investigated.

IV.2. WxAMPS-1D: A simulation tool for solar cell analysis

The primary objective of numerical modeling and simulation in solar cell research is to match model output with experimental results and evaluate the validity of proposed physical structures and geometries on cell performance. The term Analysis of Microelectronic and Photonic Structures-One Dimensional is represented by the abbreviation AMPS-1D. Professor Stephen Fonash and his students at Pennsylvania State University, in collaboration with the Electric Power Research Institute (EPRI), developed AMPS-1D. The AMPS-1D. The program is designed to simulate and model the behavior of multijunction solar cells.

Over 200 organizations worldwide have used AMPS-1D for solar cell design, as it has proven to be a highly effective tool for understanding device behavior and physics in single-crystal, polycrystalline, and amorphous structures [238,239]. In recent years, it has been extensively utilized for the analysis and modeling of thin-film photovoltaic cells [240]. By modeling their performance under various conditions, AMPS-1D enables engineers and researchers to design and improve a wide range of structures, including semiconductor devices, light-emitting diodes, and solar cells. Because AMPS-1D is one-dimensional, it is especially well-suited for studying layered structures and understanding their behavior at the microscopic level.

IV.3. Simulation and parametrization of input structures

Input parameters for calculations using the AMPS-1D software include surface recombination velocities, spectral irradiation, barrier heights, Schottky barrier heights, and the optoelectronic properties of the layers that make up the structure to be simulated [241–243]. Four fundamental panels make up the primary AMPS-1dD interface, and each one provides essential qualitative data that defines the character of the simulation (*Fig. IV.1*).

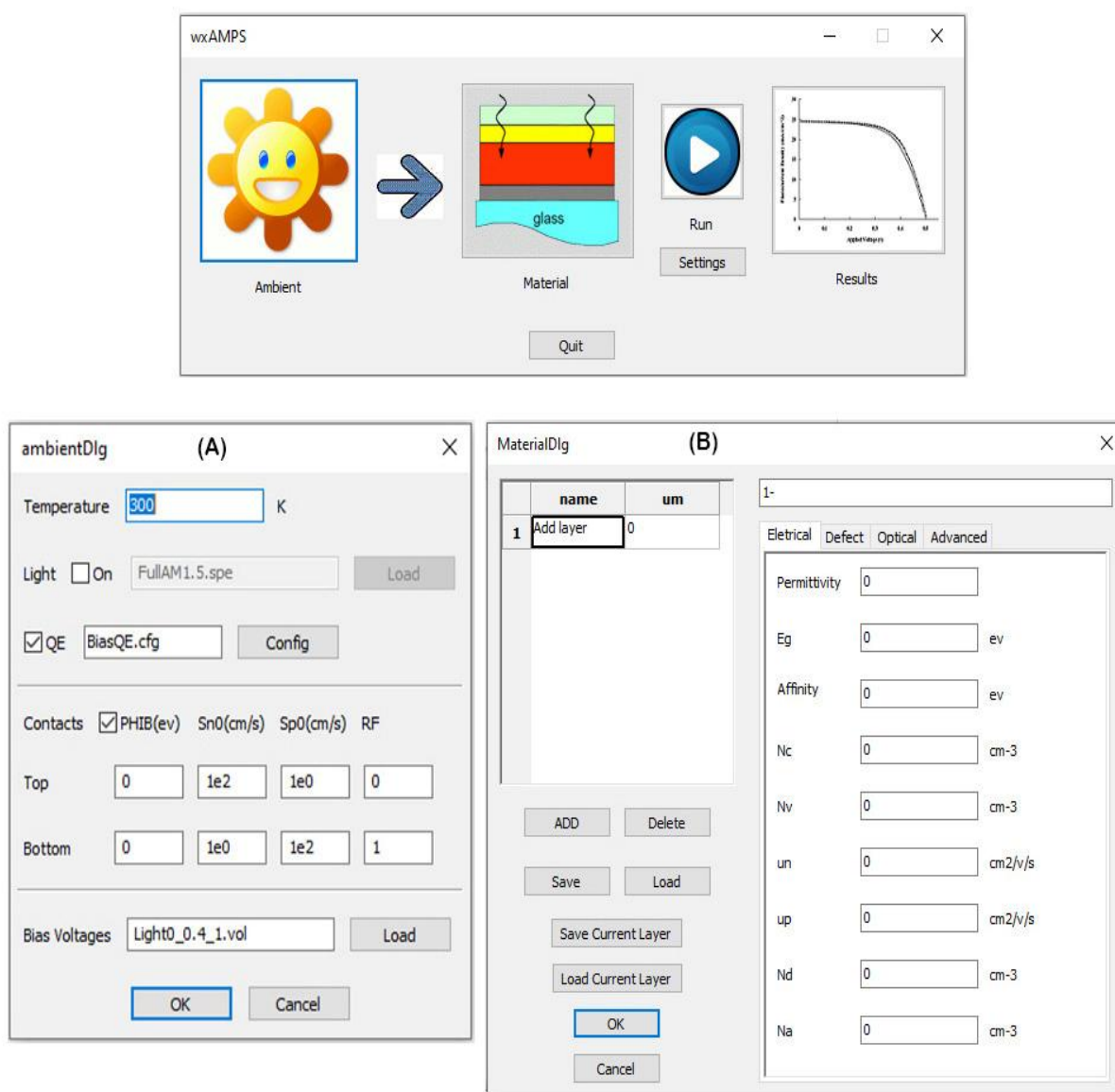


Fig. IV.1: AMPS-1D interface: (A) Environmental factors and (B) electrical input specifications.

Chapter IV: Solar cell application within the studied materials by using (AMPS-1D)

Light and temperature can be adjusted through the environmental conditions interface, as illustrated in [Fig. IV.1\(A\)](#) for AMPS-1D. To examine their impact on the photovoltaic cell's performance, the temperature was set to room temperature (300 K), with the option to select either illuminated (light) or dark conditions.

The interface for the material's optoelectronic characteristics for each layer that makes up the simulated structure including electronic, optical, and defect properties, is shown in [Fig. IV.1\(B\)](#). Therefore, to achieve the best efficiency, we can examine how the thickness and doping levels of each layer affect the electrical characteristics of the PV cell after selecting the solar cell model to simulate.

IV.4. Standard terms and conditions for simulation

We considered the lighting conditions during the simulations carried out using the simulation program described in this chapter. Photovoltaic and solar energy research frequently employs the AM1.5 standard spectrum. The spectral data in this file contains observations in W/m^2 across a variety of wavelengths.

IV.5. Proposed photovoltaic cell architecture

Based primarily on the CaSiSe_3 material examined in the preceding section using the Wien2k algorithm, we selected two different types of layered configurations for solar cells. This section expands on the results of the previous analysis.

IV.5.1. Proposed ZnO/CdS/CaSiSe_3 heterostructure:

In this proposed cell, we have incorporated a specific arrangement of three layers. The top layer consists of n-type zinc oxide (ZnO), which is commonly used as the electron transport layer (ETL). This is connected to an n-type cadmium sulfide (CdS) layer, followed by a third layer of p-type perovskite chalcogenide material (CaSiSe_3), which is a highly efficient photon absorber, as we mentioned in the previous section. [Fig. IV.2](#) displays the current-voltage (I-V) and power-voltage (P-V) characteristics generated by the ZnO/CdS/CaSiSe_3 , optimized device while operating under the AM1.5G spectrum and one sun illumination. We also summarize the relevant PV parameters, such as open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), fill-factor (FF), and efficiency (η).

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In the simulation of this Heterostructure, the ZnO layer parameters-thickness, bandgap energy, and dielectric constant are set to 0.80 μm , 3.7 eV, and 9, respectively. Similarly, for the CdS layer, the assigned values are 0.05 μm , 2.4 eV, and 10. additionally, an absorption layer with a thickness of 1 μm is incorporated.

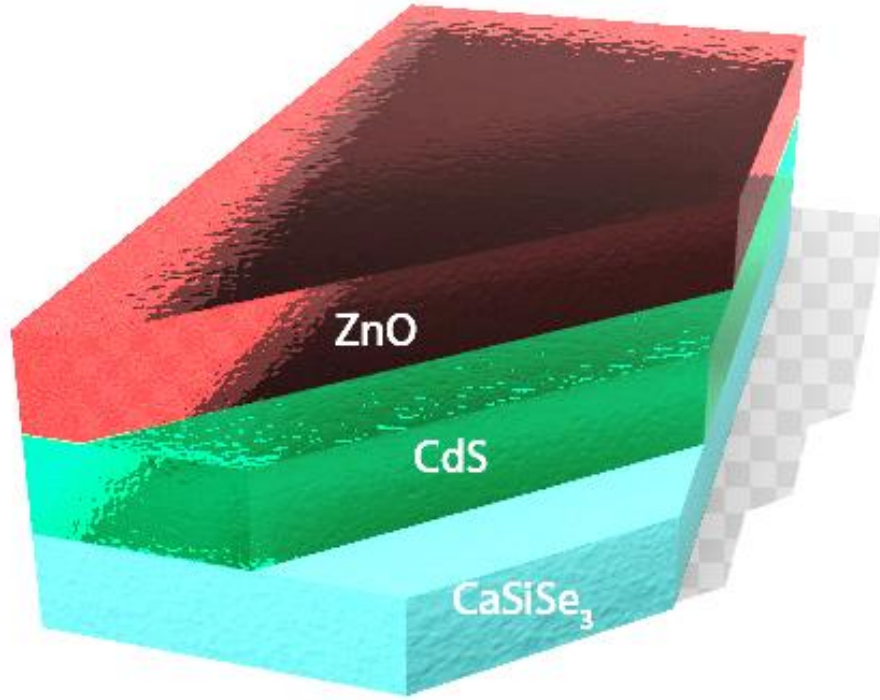


Fig. IV.2: Architected of CaSiSe_3 heterostructure solar cells module.

Table IV.1: Used parameters in the simulation of ZnO/CdS/ CaSiSe_3 devices.

	<i>ZnO</i> [244]	<i>CdS</i> [245]	<i>CaSiSe₃</i>
$\chi_e(\text{eV})$	4.5	4.30	4.5
$N_c(\text{cm}^{-3})$	2.22×10^{18}	2.20×10^{18}	3.50×10^{21}
$N_v(\text{cm}^{-3})$	1.80×10^{19}	1.80×10^{19}	2.5×10^{19}
$\mu_n(\text{cm}^2/\text{V.s})$	100	100	100
$\mu_p(\text{cm}^2/\text{V.s})$	25	25	100
$N_d(\text{cm}^{-3})$	1.0×10^{18}	1.15×10^{17}	0
$N_a(\text{cm}^{-3})$	0	0	1.0×10^{15}

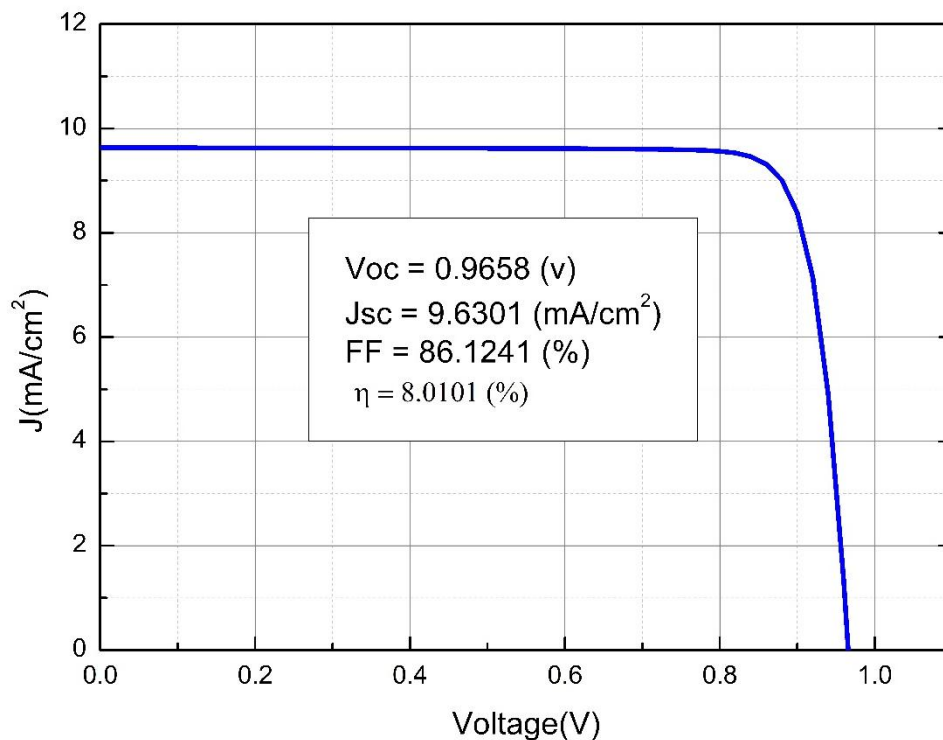


Fig. IV.3: Current-Voltage characteristics $ZnO/CdS/CaSiSe_3$.

IV.5.2. Design of a $CaSiSe_3$ -based perovskite/Silicon tandem solar cell

In this section we explore the structural design of tandem solar cell, which consist about the integration of a perovskite chalcogenide-based ($CaSiSe_3$) absorber layer as the upper cell that captured the high-energy photons, together with a crystalline silicon lower cell that absorbs the lower-energy photons, as shows in [Fig. IV.4](#). The initial target for this deigned is to enhance the efficiency of photovoltaic cells. [Fig. IV.5](#) displays the optimized $CaSiSe_3$ -based perovskite with a silicon substrate, illustrating the current-voltage and power-voltage characteristics under the AM1.5G spectrum at one sun illumination. Additionally, important PV parameters such as open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), fill-factor (FF), and efficiency (η) are presented.

The thickness of $CaSiSe_3$ solar cell layers is set to 300 nm. The parameters of the silicon layer-thickness, bandgap energy, and dielectric constant—are set to 20 nm, 1.12 eV, and 3.8, respectively.

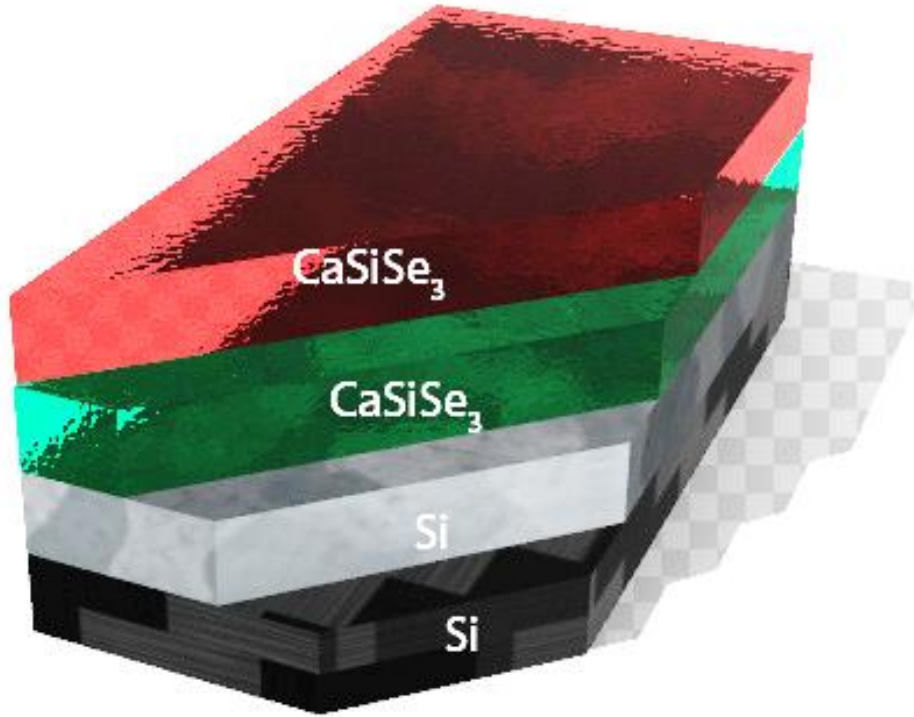


Fig. IV.4: High-performance Tandem solar cells based on CaSiSe_3 perovskite on Silicon.

Table IV.2: Electrical and optical parameters of different layers of CaSiSe_3 -based perovskite on Si.

	CaSiSe_3	CaSiSe_3	Si [246]	Si [246]
$\chi_e(\text{eV})$	3.9	3.8	3.8	3.7
$N_c(\text{cm}^{-3})$	2.76×10^{18}	2.76×10^{18}	2.51×10^{20}	2.51×10^{20}
$N_v(\text{cm}^{-3})$	3.9×10^{19}	3.9×10^{19}	1.04×10^{19}	1.04×10^{19}
$\mu_n(\text{cm}^2/\text{V.s})$	1520	1520	10	10
$\mu_p(\text{cm}^2/\text{V.s})$	1540	1540	1	1
$N_d(\text{cm}^{-3})$	0	1×10^{12}	1×10^{19}	0
$N_a(\text{cm}^{-3})$	1×10^{12}	0	0	1×10^{19}

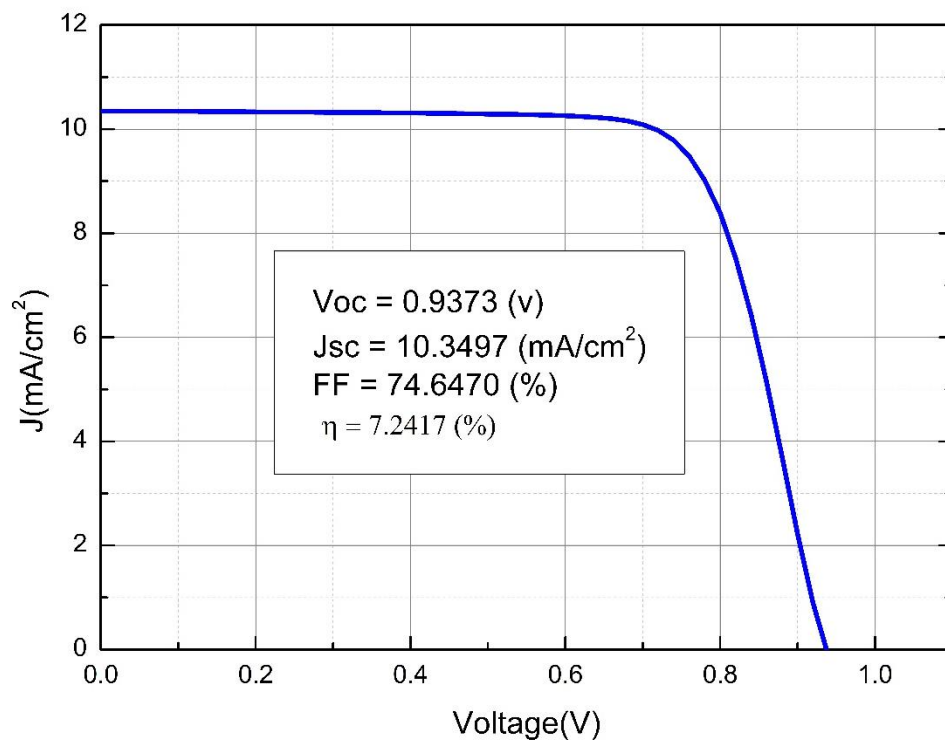


Fig. IV.5: Current-Voltage characteristics of CaSiSe₃-based perovskite on Silicon.



Conclusion and prospects

Conclusion and prospects

This work examines perovskite materials CaSiX_3 , where X equals S, Se, or Te, in an orthorhombic structure (Pnma/62). We present the results from calculations on these materials' structural, electrical, elastic, optical, and thermoelectric properties. Using the FP-LAPW method, we employed the WIEN2k code to analyze the electronic structure of the materials. To optimize the exchange-correlation potential, we utilized the TB-mBJ and PBE-GGA approximations.

Goldschmidt's tolerance and octahedral factors show that the perovskite under study are structurally stable. Regarding the structural properties, the results of the structure optimization calculated using the PBE-GGA approach indicated that substituting sulfur with selenium or tellurium increased the lattice parameter while maintaining the thermodynamic stability of these materials, as demonstrated by the obtained formation energy.

A comparison of the phonon dispersion revealed that the entire integration path of the Brillouin zone exhibited no negative frequencies for CaSiX_3 ($Y = \text{S}$ or Se), indicating that the structure is stable for these compounds. In contrast, the CaSiTe_3 compound displayed different behavior, characterized by the presence of imaginary phonon frequencies.

The fact that the values of C_{11} and C_{22} are much lower than C_{33} implies that the crystal is more resistant to failure along the z-axis than along the x- and y-axes. Additionally, the (001) plane's shear strength is greater than that of the (100) and (010) planes, as indicated by the lower values of C_{44} and C_{55} in comparison to C_{66} for CaSiX_3 ($Y = \text{S}$ or Te), but for CaSiS_3 is high according to the (010) plane. Pugh's modulus ratio and Poisson's ratio trends indicate that CaSiS_3 is brittle at room temperature.

The computed elastic moduli—bulk modulus (B), Young's modulus (E), and shear modulus (G)—all confirm this finding and attest to the material's ability to undergo plastic deformation under ambient circumstances. Additionally, the anisotropic indices that are obtained from the differences in Young's modulus along different crystallographic axes highlight the material's intrinsic elastic anisotropy.

Analysis of electronic structures reveals that TB-mBJ functionals increase their indirect fundamental bandgap compared to PBE-GGA, with the values rising from 0.790 eV to 3.020 eV for CaSiS_3 and from 0.107 eV to 1.712 eV for CaSiSe_3 . Metallic behavior can be seen through the overlap between the valence and conduction bands and the band gap of 0 eV at the Fermi level in

Conclusion and prospects

the electronic properties of the CaSiTe_3 perovskites using the PBE-GGA and TB-mBJ approach, and confirmed with the HSE₀₆ (0.05 eV). This is distinguished by the $\text{Te}_{-3s/3p}$ states' preponderant contribution and the X_p states ($X = \text{S, Se, or Te}$) minimal participation in the valence band (BV) and conduction band (BC).

In our analysis of the optical properties of these perovskites, we also calculate the dielectric function and absorption coefficient. The findings indicate that CaSiS_3 shows strong optical absorption in the ultraviolet range, while CaSiSe_3 absorbs in the visible red and near-infrared regions. Both materials demonstrate low reflectivity and can absorb electromagnetic energy outside the visible spectrum along the XX, YY, and ZZ structural directions. These properties make chalcogenide perovskites promising candidates for optoelectronic, photovoltaic, and tandem solar cell applications.

We examined the fundamental thermoelectric characteristics in relation to temperature and charge carrier concentration using the Boltzmann transport model. Our calculations indicate that the materials analyzed demonstrate a transition from p-type to n-type conduction, while consistently exhibiting high thermopower in all assessments. These results endorse the potential of CaSiX_3 ($Y = \text{S or Se}$) compounds for thermoelectric applications.

The prospects for this work are numerous. In particular, the prospects for this work are numerous. In particular, we aim to study CaSiX_3 ($Y = \text{S or Te}$) materials, either through doping or alloying, to achieve direct gaps while maintaining materials stability, with the objective of simulating tandem solar cells.



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