11-2023

FIRST PRINCIPLES INVESTIGATION OF ENERGY HARVESTING MATERIALS FOR GREEN ENVIRONMENT

Mehreen Javed

UAEU

جامعة الإمارات العربية المتحدة
United Arab Emirates University

DOCTORATE DISSERTATION NO. 2023: 43

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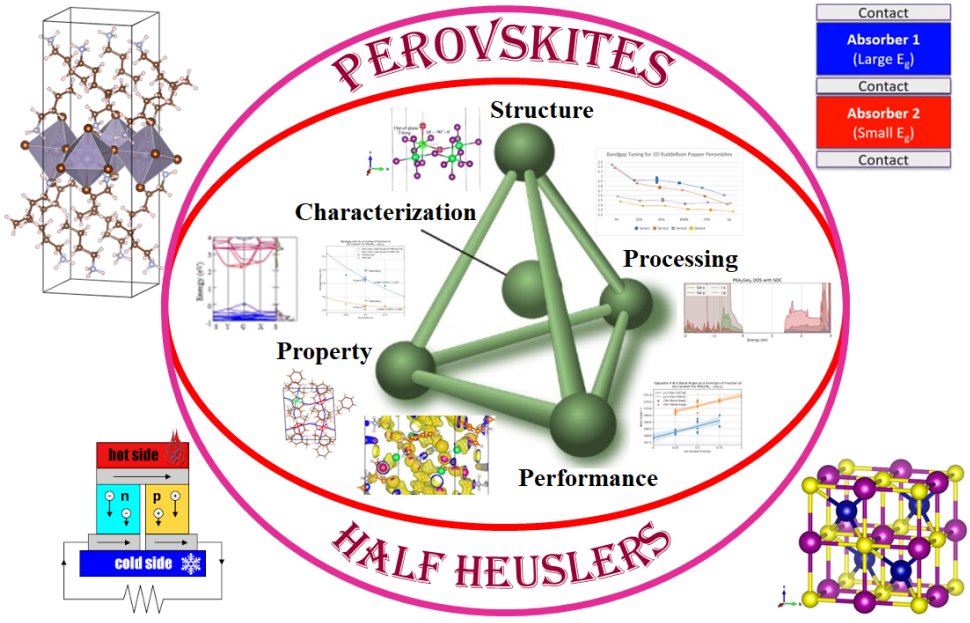

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Mehreen Javed

This dissertation is submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

November 2023

United Arab Emirates University Doctorate Dissertation
2023: 43

Cover: Computational investigation of energy harvesting materials; perovskites and half-heuslers

(Photo By: Mehreen Javed)

Print: University Print Service, UAEU 2023

Declaration of Original Work

I, Mehreen Javed, the undersigned, a graduate student at the United Arab Emirates University (UAEU), and the author of this dissertation entitled "*First Principles Investigation of Energy Harvesting Materials for Green Environment*", hereby, solemnly declare this is the original research work done by me under the supervision of Prof. Maamar Benkraouda, in the College of Science at UAEU. This work has not previously formed the basis for the award of any academic degree, diploma or a similar title at this or any other university. Any materials borrowed from other sources (whether published or unpublished) and relied upon or included in my dissertation have been properly cited and acknowledged in accordance with appropriate academic conventions. I further declare that there is no potential conflict of interest with respect to the research, data collection, authorship, presentation and/or publication of this dissertation.

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Abstract

The cutting-edge research of materials enables the discovery of novel energy harvesting materials. In this project the structural, electronic, magnetic, thermodynamic, thermoelectric, and optical properties of different energy harvesting materials are studied. The main objective of this work is primarily to study thermoelectrically efficient half-heuslers and photovoltaically active perovskites. Variant schematics of innovative compounds with defect introduction are investigated. The compositionally altered compounds designed by introducing crystallographic defects in terms of substitutional or interstitial dopants, offer new trends of material properties. To accomplish the task, Density Functional theory based computational packages (VASP and Wein2K) are used. Using defect and strain engineering, this study explores thermoelectric and photovoltaic properties. We have explored state-of-the-art features of defect tolerance, quantum and dielectric confinement, low effective masses, and high mobility in perovskites with half-metallic and thermally stable half-heuslers exhibiting high figure of merit. Our goal is to computationally design and study half-Heuslers and perovskites for thermoelectric, solar applications, and green energy productions. The computational simulations and associated results are consistent with the previous studies to give a better understanding of the perovskites and half-heuslers.

Keywords: Density Functional Theory, Half-Heuslers, Perovskites, Solar Cells, Dopants.

Title and Abstract (in Arabic)

دراسة المبادئ الأولى لمواد حصاد الطاقة من أجل بيئة خضراء

الملخص

يتيح البحث المتطور للمواد اكتشاف مواد جديدة لجمع الطاقة. في هذا المشروع تتم دراسة الخصائص الهيكلية والإلكترونية والمغناطيسية والديناميكية الحرارية والحرارية والبصرية لمواد حصاد الطاقة المختلفة. الهدف الرئيسي من هذا العمل هو في المقام الأول دراسة مركبات نصف هيوسلر ذات الكفاءة الحرارية الكهربائية والبيروفسكايت النشطة ضوئيًا. تم دراسة المخططات المتنوعة للمركبات المبتكرة مع إدخال العيوب. تقدم المركبات المعدلة تركيبيًا والتي تم تصميمها عن طريق إدخال عيوب بلورية من حيث المنشطات البديلة أو الخلالية، اتجاهًا جديدًا لخصائص المواد. لإنجاز المهمة، تم استخدام الحزم الحسابية القائمة على نظرية الكثافة الوظيفية (VASP وWein2K). باستخدام هندسة العيوب والإجهاد، تستكشف هذه الدراسة الخصائص الكهروضوئية والكهروضوئية.لقد استكشفنا أحدث الميزات لتحمل العيوب، والحبس الكمي والعازل، والكتل الفعالة المنخفضة، والتنقل العالي في البيروفسكايت مع نصف هوسلر نصف معدني ومستقر حرارياً يُظهر درجة عالية من الجدارة.هدفنا هو تصميم ودراسة نصف هيوسلر والبيروفسكايت حسابيًا للتطبيقات الكهروحرارية والطاقة الشمسية وإنتاج الطاقة الخضراء. تتوافق عمليات المحاكاة الحسابية، إلى جانب النتائج التي تم الحصول عليها، مع الدراسات السابقة لإعطاء فهم أفضل للبيروفسكايت ونصف الهيسولرز.

مفاهيم البحث الرئيسية: نظرية الكثافة الوظيفية، نصف الهوسلر، البيروفسكايت، الخلايا الشمسية، الدوبانت.

List of Publications

I. Javed, M., Sattar, M.A., Benkraouda, M., Amrane, N., Najar, A., (2023). Strained induced metallic to semiconductor transitions in 2D Ruddlesden Popper perovskites: A GGA+ SOC approach. Applied Surface Science, 627, 157244. https://doi.org/10.1016/j.apsusc.2023.157244

II. Javed, M., Noureddine, A., Benkraouda, M., (2023). Band gap tailoring with octahedral distortion and bader charge analysis for 2D-Ruddlesden–Popper monolayer tin halide perovskites. Materials Science in Semiconductor Processing, 162, 107490. https://doi.org/10.1016/j.mssp.2023.107490

III. Javed, M., Benkraouda, M., Amrane, N., (2022). Theoretical investigation of octahedral tilting and bandgap non-linearity in monolayer Ruddlesden-Popper A2Pb1-xGexI4 perovskites. International Journal of Energy Research, 46, 18588–18608. https://doi.org/10.1002/er.8474

IV. Javed, M., Sattar, M.A., Benkraouda, M., Amrane, N., (2022). First-principles investigations on the structural stability, thermophysical and half-metallic properties of the half-Heusler CrMnS alloy. Optical and Quantum Electronics, 54, 1–22.

V. Javed, M., Sattar, M.A., Benkraouda, M., Amrane, N., (2020). Structural and mechanical stability, lattice dynamics and electronic structure of the novel CrVZ (Z= S, Se, & Te) half-Heusler alloys. Materials Today Communications, 25, 101519.

Author's Contribution

The contribution of Mehreen Javed to the papers included in this dissertation was as follows:

I. Performed a leading role in planning the requisites tasks and goals of project.
II. Actively learned the computational packages, had primary role for performing the computational calculations, handling, and plotting output-data, with the interpretation of results.

III. Individual responsibility for solving enfaced problems, writing manuscripts, reviewing journal comments, and publishing manuscripts.

IV. Presented work in numerous national and international conferences.

Author Profile

Mehreen Javed, a computational physicist on an exhilarating journey towards her Ph.D. in Physics from 2019 to 2023. I, Mehreen Javed, have been blessed with the prestigious Ph.D. fellowship grant from the esteemed United Arab Emirates University, recognizing my unwavering dedication and potential in the field.

With over a decade of research experience, I have devoted myself to solving various computational problems, unraveling the captivating properties of leading energy materials. Through my theoretical investigations, I aim to guide and revolutionize the photovoltaic industry, shedding light on the most crucial research and commercial challenges we face.

During my Master of Philosophy in Physics, I had the immense honor of receiving the coveted Gold Medal for my exceptional educational performance. It was a true testament to my passion and hard work in the field. I take great pride in my research contributions, with my name gracing the pages of top-tier journals as the first author. These publications have been recognized among the top 5%, 10%, and 15% in their respective fields.

Throughout my Ph.D. journey, I have continued to make significant strides in my research endeavors. I am thrilled to share that I have already published seven impactful papers in well-reputed journals, further solidifying my position as a trailblazer in the scientific community. Alongside my research, I completed my coursework with distinction, achieving a remarkable CGPA of 4.0. Additionally, I had the opportunity of attending the Ph.D. teaching academy, honing my skills as both a researcher and an educator.

To broaden my horizons and share my insights, I actively participate in Scopus-indexed national and international conferences. As both an oral and poster presenter, I have had the privilege of contributing to events such as IWAM (2022, 2023), MRS (2022), APS (2022), SICPAM (2023), and GSRC (2022, 2023). These platforms have allowed me to engage with fellow scientists and showcase my research on a global scale.

Adding to my list of achievements, I am thrilled to have won the award for the best innovative research idea during the innovation week at the United Arab Emirates University in 2022. This recognition not only highlights my creativity and ingenuity but also serves as a testament to my commitment to pushing the boundaries of scientific exploration.

I, Mehreen Javed, am truly grateful for the opportunities and experiences that have shaped my journey thus far. With each step, I am driven by a passion for knowledge, a thirst for discovery, and a desire to make a positive impact in the world of computational physics. Together, let us continue to unravel the mysteries of the universe and pave the way for a brighter future.

Acknowledgements

I extend my heartfelt gratitude to my esteemed committee for their unwavering guidance, support, and assistance throughout the preparation of my dissertation. A special mention goes to my advisor, *Prof. Maamar Benkraouda*, whose mentorship has been invaluable in strengthening both my professional and personal skills. His continuous motivation and affection have instilled in me the confidence to explore new horizons and excel in my endeavors. I am also grateful to my co-supervisor *Prof. Noureddine Amrane* for his valuable time and guidance during my Ph.D. journey.

I would like to express my sincere appreciation to all the teachers who imparted their knowledge and wisdom during my Ph.D. courses. Their expertise and dedication have played a significant role in shaping my academic journey.

To my beloved parents and siblings, I am forever indebted to your unwavering support and love. It is because of your encouragement and belief in me that I have been able to pursue and fulfill my dreams. Your presence in my life has given me the strength to face challenges head-on.

I am humbled and grateful for the opportunities and blessings that have come my way. With the guidance of Allah and the support of my loved ones, I am committed to utilizing my skills and knowledge to contribute to the betterment of society.

Dedication

To my beloved parents

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List of Abbreviations

DFT	Density Functional Theory
HH	Half Heuslers
HOIP	Hybrid Organic Inorganic Perovskites
HOMO	Highest Occupied Molecular Orbitals
LUMO	Lowest Unoccupied Molecular Orbitals
PSCs	Perovskites Solar Cells
PV	Photovoltaic
SOC	Spin Orbit Coupling
TE	Thermoelectric

Chapter 1: Introduction

1.1 Overview

Energy is the main fuel for life. Since for ages, human energy demands are being fulfilled by trivial carbon-based resources (Bei & Wang, 2023). Conversely, these depleting fossils fuels with outrageously high cost and hazardously fatal environmental concerns require an immediate shift towards replenishable, clean, and affordable energy alternatives (Ali et al., 2023). Naturally available renewable energy resources can combat unprecedented current energy shortfall. Nonetheless, the technological limitations for renewable energy conversions and storages are significant bottlenecks which has directed scientific research to investigate the causes, effects, and solutions (Shang et al., 2023). This thesis focuses on how science, technology, and innovation can assist to promote the usage of energy harvesting materials in global energy crisis.

1.2 Statement of the Problem

Solar energy is the most crucial and commonly available renewable energy resource (Obaideen et al., 2023). Annually about 23000 TW solar energy hits from sun to earth out of which only 16 TW is used. About 60% of solar energy is going unused which can serve as a key for global decarbonization by providing 50% of sustainable energy in 2050. Besides, a huge amount of heat energy is discarded and goes unused during combustion or industrial processes. The efficient usage and restoration of natural and synthetic energy from light or waste-heat is the main goal of thermoelectric (TE) and photovoltaic (PV) industries. To achieve this objective, the investigation of innovative energy harvesting materials including Half-Heusler and Perovskites is an indispensable strategy. Commercially available Si-based solar cells are expensive and have limited threshold efficiency up to 30%; however, a revolutionary leap of perovskites-based solar cells have surpassed the edged efficiency using Tandem based solar cells. Defect and strain engineered 2D-perovskites offer desirable bandgaps to enhance photovoltaic conversion of solar cells. For energy storage and spintronic applications, a new class of half-heuslers is introduced offering 100% spin-polarization, reasonable bandgap, and high thermal stability. To help reduce carbon emission and reuse waste heat both these

energy harvesting materials find real life applications, in electricity generation and waste-heat recovery, with vast scope of interests in practical world.

1.3 Research Objectives

The main research objectives aimed in this thesis are listed as follows.

1. Investigate the electronic and structural properties of half-Heusler and perovskite materials using density functional theory (DFT) simulations.
2. Design and optimize energy harvesting devices based on half-Heusler and perovskite materials, including solar cells, thermoelectric generators, and fuel cells.
3. Investigate the stability and durability of half-Heusler and perovskite materials under various environmental conditions using DFT simulations, such as exposure to moisture, heat, and light.
4. Develop new materials and strategies for improving the performance and stability of energy harvesting devices based on half-Heusler and perovskite materials.
5. Investigate the effect of doping on the electronic and structural properties of half-Heusler and perovskite materials and optimize their properties for energy harvesting applications.
6. Explore new materials and strategies for improving the scalability and efficiency of energy harvesting technologies based on half-Heusler and perovskite materials.
7. Approximately evaluate the performance of energy harvesting devices based on half-Heusler and perovskite materials under real-world operating conditions.
8. Develop a comprehensive understanding of the fundamental properties of half-Heusler and perovskite materials and their interactions to design hybrid PV-TE devices.

In Figure 1, a model diagram illustrates the complete schematic of the current thesis depicting how the input from literature, database, and papers helped to design new perovskites and half-heuslers by pairing suitable elements from periodic table. Considering the challenges of toxicity, stability, and efficiency, DFT based simulations in VASP and WEIN2k packages were performed. Results were plotted using Origin and Python codes. Numerous important calculated properties were published in reputed journals.

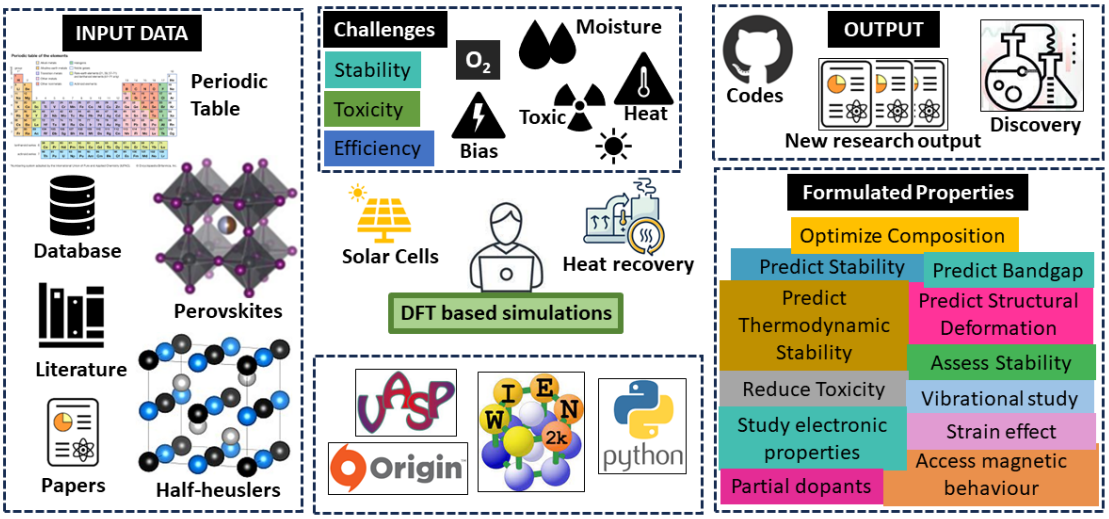

Figure 1: The model diagram illustrates the thesis workflow.

1.4 Relevant Literature

A concise yet comprehensive overview of two key energy harvesting materials that are the focus of our exploration in this work including Half-heuslers and perovskites is presented. With details about their discovery, structure, properties, and applications we briefly shed light on how these fascinating materials hold great potential in realm of energy devices.

1.5 Half-Heuslers

The state-of-the-art Half-Heusler (HH) alloys were 1st discovered by German mining engineer Fredrick Heusler ("Personal and University News 'Personal- und Hochschulnachrichten'.," 1936). HH as promising thermoelectric (TE) materials can transform dissipated waste heat into useful, environmentally benign, and less costly form of energy (electricity) for vast industrial applications. In combustion, hot gases are exhausted at very high temperature (600K-1000K) thus forming a hot-end of thermoelectric device. HH with high thermal stability can transfer this heat energy into electricity. Most generally known TE candidate includes PbTe, oxides, skutterudites, and half-Heuslers. The commercial limitations of toxicity and low thermal stability for the PbTe and skutterudites favor HH materials as promising TE contenders for abjuration of common deficiencies (Huang et al., 2016).

1.5.1 Structure

Half heuslers with chemical formula of ABX possess cubic-like non-centrosymmetric symmetry with $F\bar{4}3m$ space group; they are formed by interpenetrating face-centered-cubic (FCC) sublattices (Kawasaki et al., 2022). A structure illustration for investigated HH material is shown in Figure 2, where the unit cell of half-Heusler CrMnS alloy in the $C1_b$ structure display three intercrossed FCC sublattices with distinct atoms located at 4a (1/4, 1/4,1/4), 4b (1/2, 1/2,1/2) & 4c (0,0,0), with one empty 4d (3/4, 3/4,3/4) site. In the left visual illustration, the atoms Mn, Cr, and S are represented with purple, blue, and yellow colors, respectively. However, the right illustration of half-heuslers CrVZ (Z= S, Se, Te) have similar structure as CrMnS with green, purple, and blue atoms of Z, V, and Cr respectively.

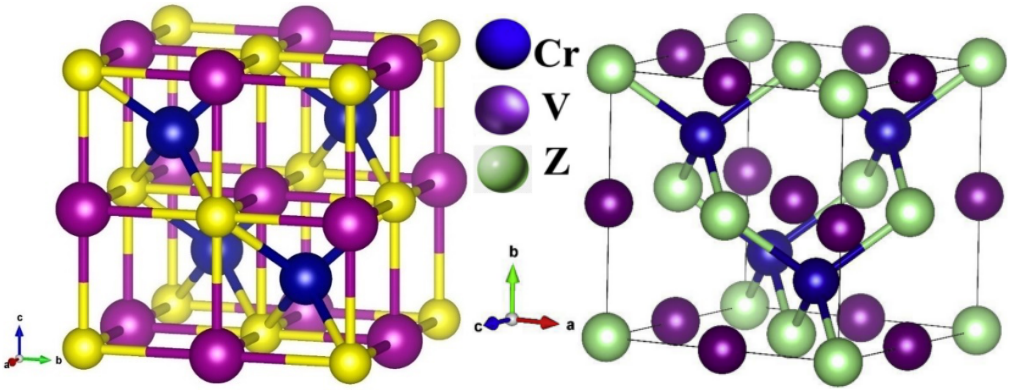

Figure 2: Unit cell of the half-Heusler (Left) CrMnS and (Right) CrVZ alloys.

1.5.2 Properties

With colossal spin-polarization, half-metallic ferromagnetism, mechanical strength and high Curie temperature, and large thermal conductivity, HH alloys promise bundle of promising structural, magnetic, electronic, mechanical, thermodynamic, vibrational, and thermoelectrical characteristics, as shown in Figure 3. In HH alloys, non-magnetic elements combine to form magnetic compound with metallic to half-metallic nature. For competitive TE technology, HH alloys are desired to have dimensionless figure of merit (ZT) greater than 1. ZT is defined by $(S^2\sigma/\kappa)$ T depending on absolute working temperature (T), electrical conductivity (σ), thermal conductivity

(κ), and Seebeck coefficient (S) parameters. A higher electrical conductivity and Seebeck coefficient with low thermal conductivity is ideal.

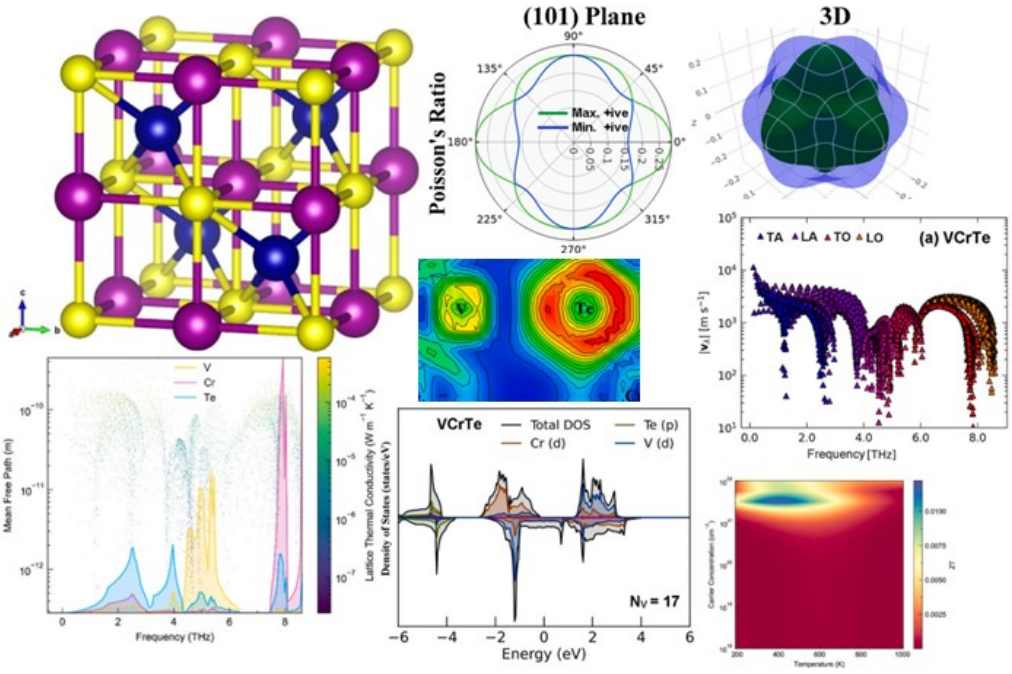

Figure 3: A few important results obtained while investigating half-heuslers alloys.

1.5.3 Applications

Stemming from the astonishing thermoelectric properties, tremendous thermal stability, and outstanding elastic properties, HH alloys are projected to inspire numerous real-life industrial applications special for waste heat recovery. Their mechanical, chemical, vibrational, and thermodynamical stability, with diverse functional properties of electrical robustness and high ZT value make semiconducting HH alloys become very attractive for power generation, spintronics, and solar cells applications.

1.6 Perovskites

Perovskites were first discovered in Ural Mountains of Russia by Gustav Rose in 1839 and named after German Minerologist Lev Perovski who found trivial inorganic perovskites $CaTiO_3$ with prototype ABX_3 structure. Since for long, inorganic 3D-perovskites has ruled the scientific research by offering promising photovoltaic properties with considerably high photoconversion efficiency. But the instability of 3D-

perovskites is an evitable issue that is required to get resolved in order to take complete advantages of photovoltaic capability. Another challenge is the presence of toxic lead in key lead-based perovskites. Thus, alternative lead-free perovskites are highly necessary to effectively introduce perovskites based solar commercially. These two hindrances, i.e., instability and toxicity, are the main driving force to launch a new scheming of perovskites with hydrophobic and lead-free components.

1.6.1 Structure

3D-perovskites with ABX_3 structure contains the inorganic metal cation A and B with halide anion X, and the cages of BX_6^{-4}octahedronsform a cuboctahedral coordination with B-cations. The poor stability of 3D-perovskites is handled by reducing their dimensions to 2D counterparts, which have long chains of water-resistant organic spacer cations with chemical configuration of $[RNH_3]_nA_{n-1}BX_{3n+1}$, where "n" is number of layers of corner shared octahedral cages. Depending on how octahedral cages are connected to each other, the 3D-perovskites are categorized as corner, edge, and face shared perovskites. However, in 2D-perovskites these octahedral layers are connected at corners with the organic spacer cations shielding them from moisture attack. An illustrative representation of 3D versus 2D perovskites is shown in Figure 4. These 2D-perovskites are further categorized as Ruddlesden-Popper (RP) and Dion-Jacobson (DJ) perovskites. The main distinction lies in the composition of these forms with the presence of monoamine and diamine spacer cations for RP and DJ forms, respectively. Another difference is the location of spacer cation is off centered in RP than in DJ as shown in Figure 4. Joining these octahedral cages along apical and equatorial plane resulted in the formation of perovskites crystal structure. By varying the number of octahedral layers "n", the monolayer, bilayer, and multilayer perovskites can be synthesized. When n=1, the monolayer perovskites are composed of a solitary sheet of octahedral cages, delicately nestled between the hydrophobic spacers. This arrangement provides a protective shield to the chemically active octahedrons from potential damage caused by moisture, heat, and other environmental hazards (Javed et al., 2022a).

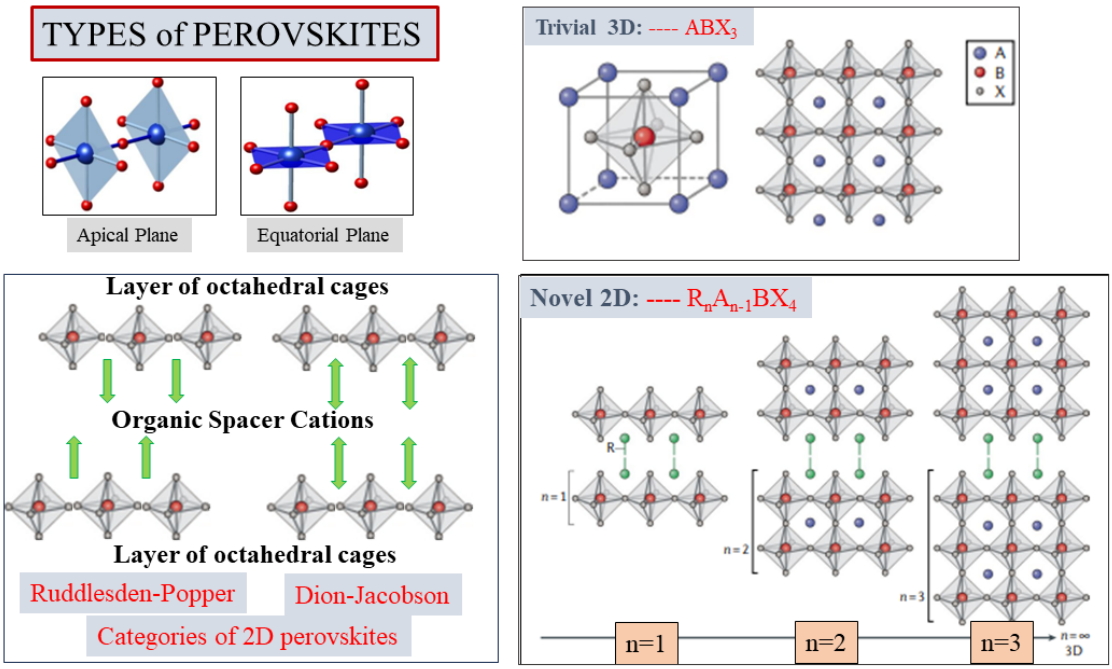

Figure 4: The 3D versus 2D perovskites show monolayer and multilayer structures.

1.6.1.1 Defect Engineering

Perovskites offer a high flexibility to tune their optoelectronics by altering the chemical scheming of constituent elements without getting their structure distorted. Using defect engineering, all sites of $[RNH_3]_nA_{n-1}BX_{3n+1}$can be replaced partially or completely to design new perovskites as shown in Figure 5. To replace toxic lead in champion perovskites; the Ge and Sn comprise the suitable option since they belong to the same group of Periodic Table, so they retain almost the same chemical properties but have no toxicity (Javed et al., 2022a). Similarly, the halide anions can be replaced partially or completely with I, Br, and Cl halide anions. For the n=1 configuration, A-site gets eliminated so with the chemical formula of RNH_3BX_4 monolayer perovskites are studied with Methylethylammonium(MA) and Phenylethylammonium(PEA) spacer cations.

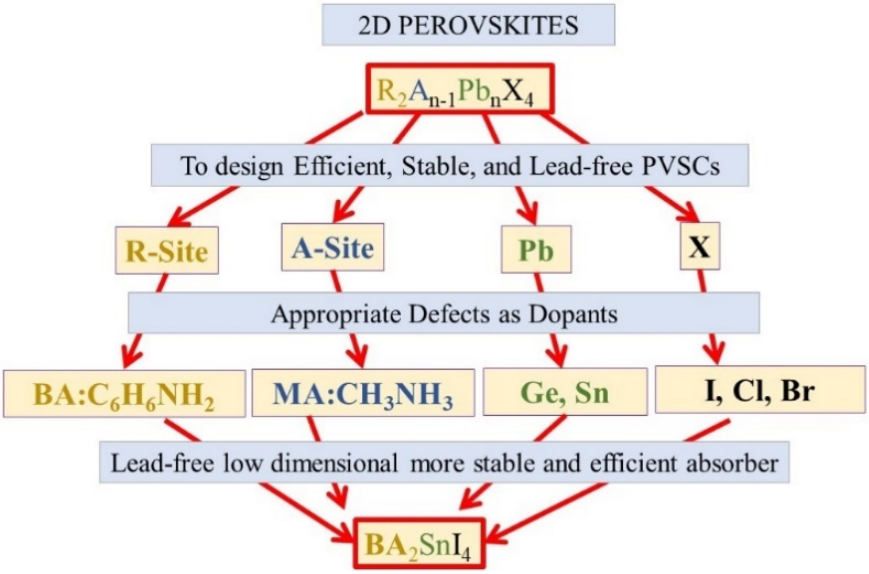

Figure 5: Schematic of defect engineering by elemental pairing adopted in this work.

1.6.1.2 Strain Engineering

Strain engineering is an advanced measure of introducing structural deformation under compression or expansion, a key to modulate electronic and mechanical properties (Javed et al., 2023b). The mechanically soft perovskites crystal structures are flexible to the applied strain as shown in Figure 6. The manipulated strained-orientation schemes play a crucial role in providing the diverse structural stability, energy-level alignment, and tunable bandgaps. Thus, highlighting the strain engineering as an incredibly efficient method in perovskite research, researchers can adjust and tune the device performance of PSCs to achieve promising optoelectronic properties (Islam et al., 2023).

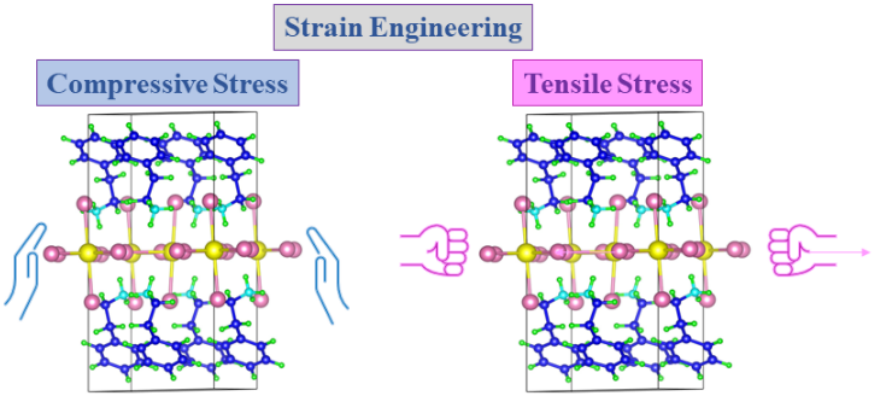

Figure 6: Compressive and tensile strains in 2D-perovskites causing structural alterations.

1.6.2 Properties

Perovskites with wonderful optoelectronic properties have proved to be a leading candidacy in the next-generation photovoltaics (Dong et al., 2023). With a range of desired inherent characteristics (including tunable bandgaps, strong light absorption-coefficients, high carrier-mobilities, large diffusion-path lengths, and long carrier-lifetimes (He & Liu, 2023), they have showed an avalanched progress in their efficiency in the last few decades, as presented in Figure 7. The single junction-based perovskites solar cells sprout with the power conversion efficiency of 3.8% (Kojima et al., 2009) have dominantly raised up to 40% by changing the solar cell setup with two or more solar cells stacked in the multijunction Tandem solar cell. By stacking the perovskites with bandgaps ranging in visible spectrum region (1.6-3.1eV), we can maximize the use of solar spectrum and enhance the efficiency (Bati et al., 2023).

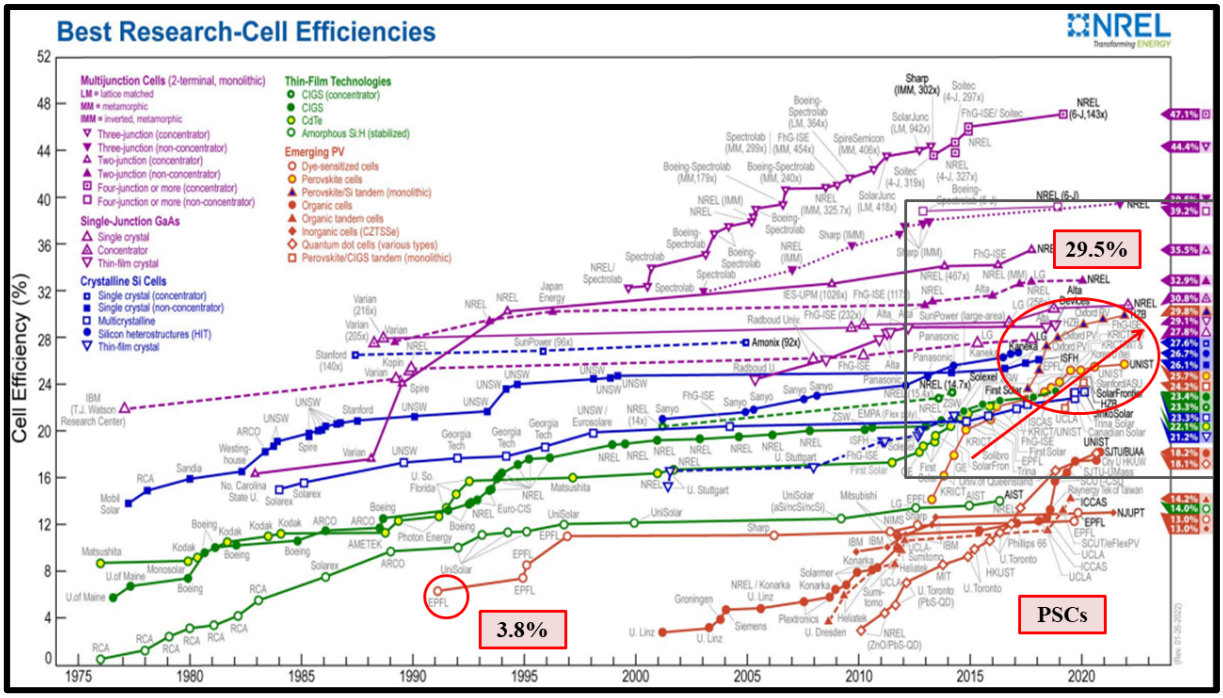

Figure 7: The time chart of solar cells showing avalanched performance of perovskites solar cells.

To solve the stability, efficiency, and toxicity issues simultaneously, we have studied 32-permutations of [R-NH_3] $Pb_{1-x}Ge_xX_4$ systems which are designed by introducing Ge (25%, 50%, 75%, 100%) to replace Pb. The consequently designed 2D-

monolayer perovskites with different spacer cation of Methyl-ethyl-ammonium and Phenyl-ethyl-ammonium with chemical formulae of ($CH_3NH_3^+$) ($C_6H_5[CH_2]_2NH_3^+$) were studied to make a comparative investigation as shown in Figure 8. With the introduction of the larger spacer cation, the bond lengths between B-cation and X-anion were observed to decrease while the bond angles between B, X, and B atoms increased, which induces a lattice alteration and octahedral inclination, responsible for the decrease in band gap under compressive stresses.

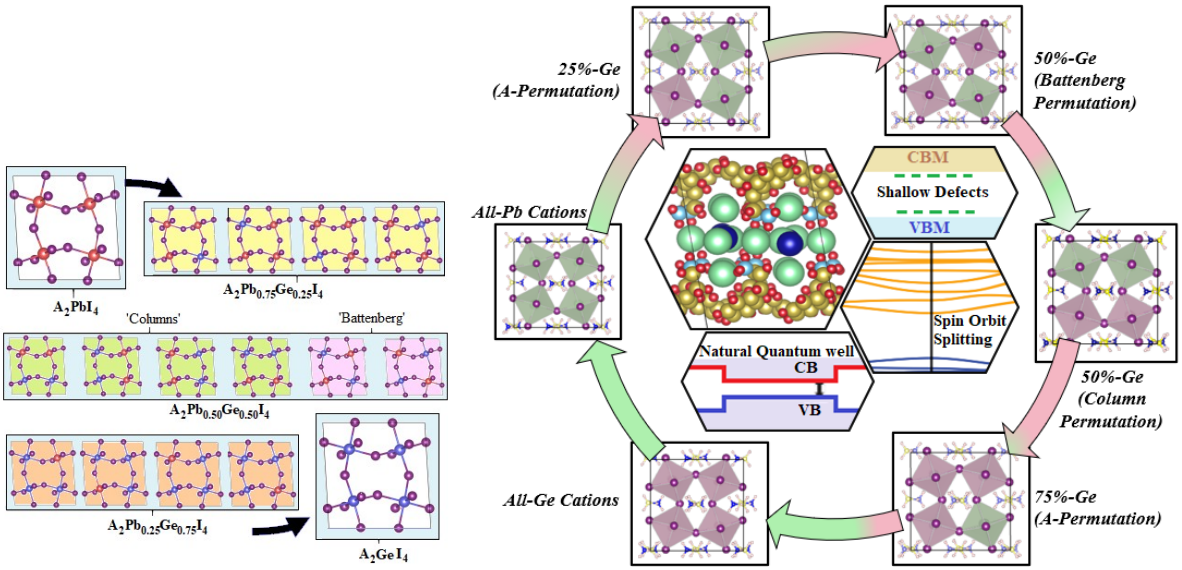

Figure 8: Partial substitution of B-cation Ge in replacement of Pb

A larger spacer cation also increases the lattice barrier energy to eradicate the structural degradation. As shown in the left panel of Figure 9, we have also studied the effect of four different spacer cations with non-toxic Tin in combination with three different halide anions. Furthermore, to study the effect of the compressional or expansional stress, we have applied the stress on 2D-perovskite through introducing a flexible atomic positioning coupled with the formation of narrow or wide-bandgap perovskites absorbers which can be assembled as sub-cells layers in multijunction all-2D-Perovskites based tandem solar cells, as shown in the right panel of Figure 9. Thus, a rational design approach was implemented to modify the optoelectronic properties by altering the organic spacer cation, inorganic cation, and anion. Our findings depict that the monolayer perovskites with distinct versatility and performance can serve as

excellent absorbers to maximize the use of light across a wider wavelength invisible-to-infrared (2.4-1.2 eV) range. With the distinguished features (such as tunable bandgaps, dielectric confinement, quantum confinement, and defect tolerance), the investigated 2D-perovskitesfind a large scope in designing efficient Tandem solar devices.

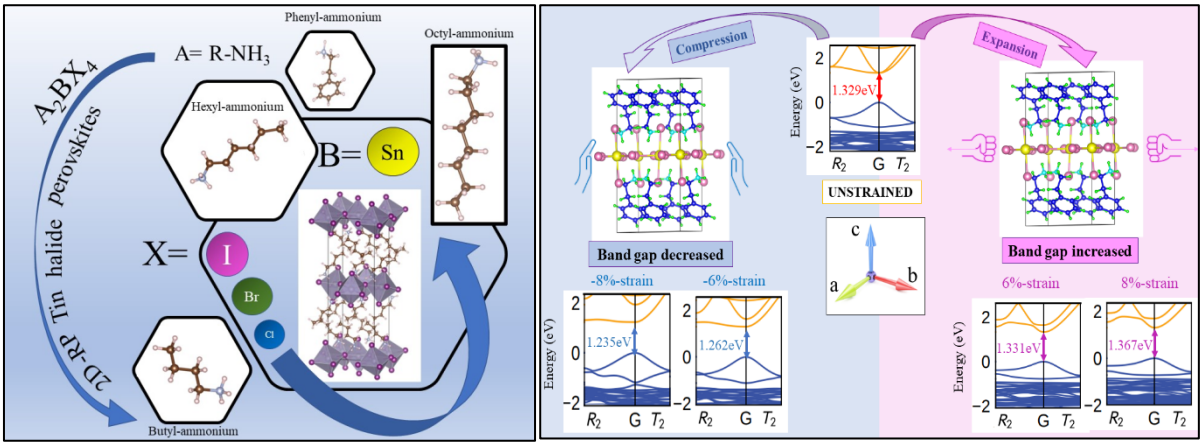

Figure 9: 2D-monolayer perovskites with defect (left) and strain (right) engineering.

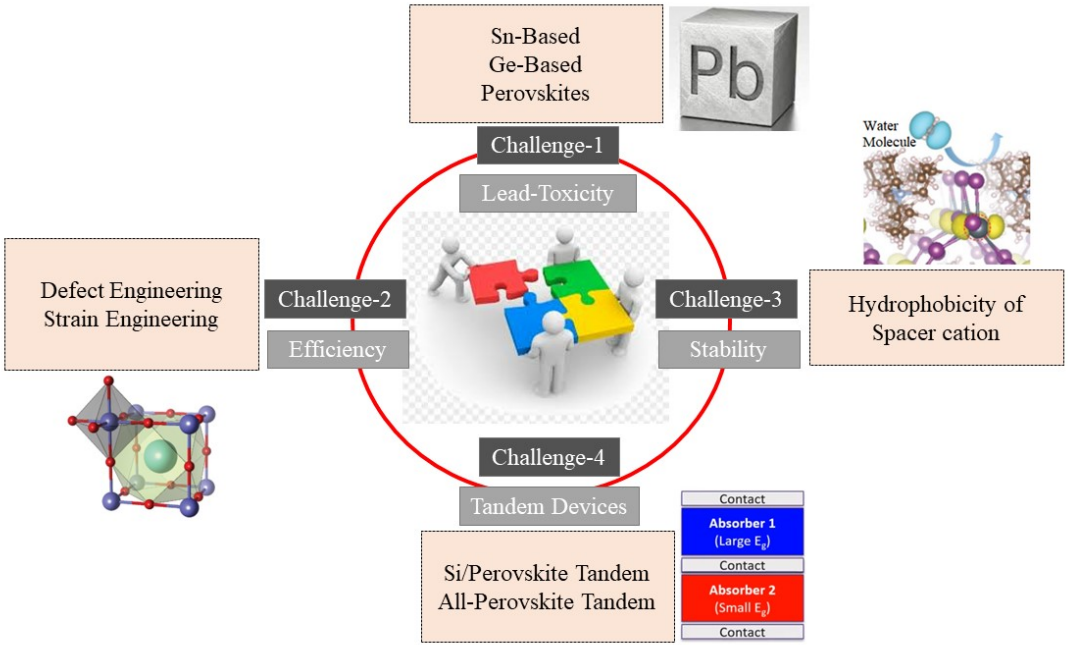

Figure 10: The challenges encountered in commercialization of perovskites solar cell.

1.6.3 Applications

As a cutting-edge scientific discovery, perovskites solar cells hold a great promise to produce cheap, sustainable, and clean energy form, thus capturing the attention of researchers to seek their practical applications at the domestic and industrial scales. Lightweight, flexibly textured, and easily installed perovskites solar cells with unique optoelectronic properties have facilitated the wide applications including building-integrated photovoltaics, solar powered transportation, space applications, battery charging, and energy storage, as shown in Figure 11. Tandem solar cell is a breakthrough innovation in perovskites photovoltaics, which combine small and large bandgaps based single junction solar cells to utilize a bigger portion of incident light energy. Perovskites with structural flexibility offer an inherent characteristic of highly tunable bandgaps, which encourages researchers to design innovative perovskites. To avoid trial-error based expensive experimental designing, the theoretical screening and investigation of lead-free perovskites with high stability and low dimension become highly useful and meaningful, which is hopeful to exhibit exclusive structure-property features endowing them with state-of-art optoelectronic efficiency and versatile functionality. But to upscale the lab-scale perovskites solar cells in the commercial applications, we need to cope with challenges (as shown in Figure 10) related to instability, lead-toxicity, low efficiency, and the design of versatile perovskites is suitable for all-perovskites, or Si/perovskites based Tandem solar cells.

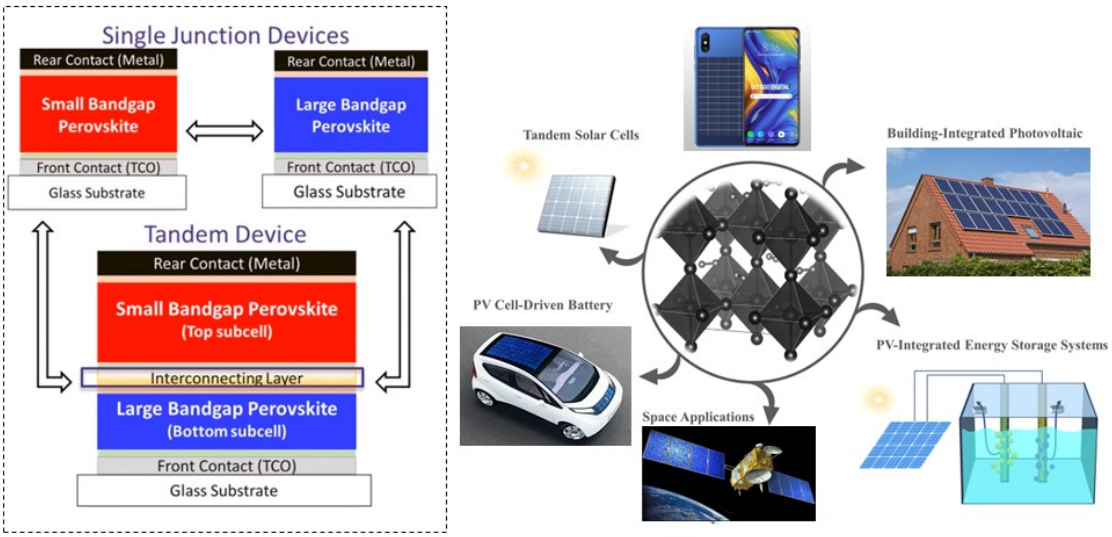

Figure 11: Illustration of Tandem solar cells with their multiple practical applications.

Chapter 2: General Discussions

2.1 Research Design

The leading energy harvesting materials have attracted relentless efforts due to their astonishing properties. To achieve the goal, different possible configurations will be sampled computationally, where two density functional theory based computational packages,WEIN-2k (Blaha et al., 2020) and Vienna ab-initio simulation package (VASP) (Hafner & Kresse, 1997), will be used to execute systematic calculations.

2.1.1 Density Functional Theory

Density functional theory (DFT) is a quantum mechanics-based tool used to solve many particles problems in materials science by establishing a good balance between computational accuracy and efficiency. According to Hohenberg-Kohn (HK) 1st-theorem, the DFT originates its name from energy functional as energy is function of electron density $n(\vec{r})$which itself is function of spatial coordinate $E\ [n(\vec{r})]$. Electron density makes the calculation computationally simpler by reducing the 3N spatial degree of freedom to only three if N is number of interacting electrons. The many-body perspective simplification to DFT perspective is picturized in Figure 12.

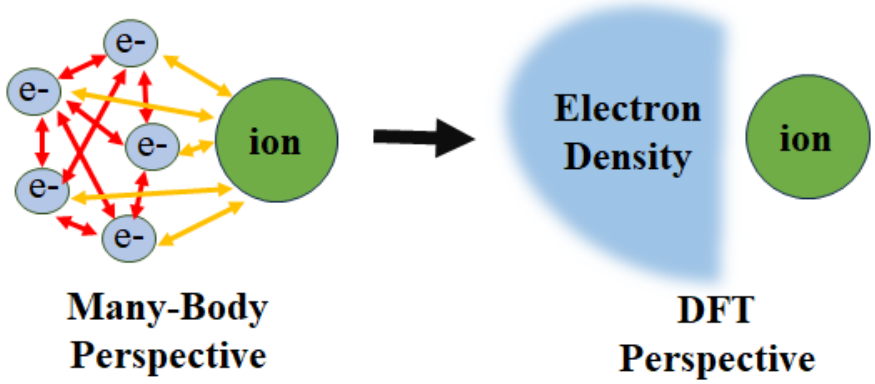

Figure 12: The many-body versus DFT perspective to treat the problem of many-particles.

The simpler form of Schrödinger equation is given in equation 1 (Harshman, 2019; Shankar, 2012), where $\hat{H}$ is Hamiltonian operator acting on ψ eigenstate and results in E energy eigen value.

$$\hat{H}\psi = E\psi \qquad \text{Eq. 1}$$

It can be easily solved for H-atom but for complex systems with many-body system to solve the many-electrons based Schrödinger equation, the Density functional theory serves an effective computational tool operated in VASP and WEIN2k packages. The extended form of Schrödinger equation is given in equation 2 (Harshman, 2019; Shankar, 2012) where total energy is divided into kinetic energy (cyan) and potential energy (red).

$$\hat{H} = \underbrace{-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2}_{\text{Kinetic Energy Terms}} \underbrace{-\sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>1}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}}}_{\text{Potential Energy Terms}} \qquad \text{Eq. 2}$$

Here, 1st term indicates the kinetic energy of interacting electrons, 2nd term is kinetic energy of interacting nuclei, 3rd term is nucleus-electron attractive potential, 4th term is electron-electron repulsive potential, and 5th term is nucleus-nucleus repulsive potential. The symbols ∇_i^2, $\vec{r}_{ij}$, and $\vec{R}_{AB}$ are defined in Eq. 3 (Harshman, 2019; Shankar, 2012).

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}, \vec{r}_{ij} = \left|\vec{r}_i - \vec{r}_j\right|, \vec{R}_{AB} = \left|\vec{R}_A - \vec{R}_B\right| \qquad \text{Eq. 3}$$

According to the Born Oppenheimer approximation, the nuclei that are three times heavier than electrons can be considered static, therefore, 2nd term in Eq. 2 vanishes. Similarly, the 5th term is also ignored for representing a constant potential operating between static nuclei. The Hohenberg- Kohn (HK) 2nd-theorem states that an electron density is associated to the ground state if it gives an energy that approaches the minimum value of ground state.

2.1.2 Kohn Sham Approach

Kohn-Sham (KS) theorem later further improved the HK theorem by replacing the static external potential of interacting many-particle electrons to a fictitious model of non-interacting electrons pertaining effective Kohn-Sham potential $V_{KS}[n(r)]$, given in Eq. 4 (Hu et al., 2021; Wang and Zhang, 2013).

$$\left(-\frac{\nabla^2}{2} + V_{KS}[n(r)]\right)\psi_i(r) = E_i\psi_i(r) \qquad \text{Eq. 4}$$

In Eq. 4, the Kohn-Sham potential $V_{\mathrm{KS}}(r)$ is also called the effective potential, which consists of external potential, Hartree potential, and exchange-correlation potential, given in Eq. 5 (Hu et al., 2021; Wang and Zhang, 2013).

$$V_{KS}(r) = V_{ex}(r) + \int \frac{n(r')}{|r-r'|} d^3r' + V_{XC}[n(r)] \qquad \text{Eq. 5}$$

Here, in Eq. 5, the term $V_{\mathrm{ex}}(r)$ is the external potential, the 2nd Hartree term represents electron-electron Columb repulsion, and V_{XC} is exchange correlation potential. The last two terms depend on electron density $n(\vec{r})$ which depend on Kohn-Sham orbitals $\varphi_i$which in return depends on effective potential, thus solving the DFT problem in self-consistent (SCF) iterations. Staring from a guess electron density, a corresponding effective potential is calculated by solving the KS equations for φ_i. From $\varphi_i$again electron density is calculated as given in Eq. 6 (Hu et al., 2021; Wang and Zhang, 2013).

$$n(r) = \sum_{i=1}^{N} |\varphi_i(r)|^2 \qquad \text{Eq. 6}$$

The resulting density is again used to calculate to new potential until electron density approaches its minimum value for which ground state energy is obtained and convergence is reached. The SCF cycle is shown in Figure 13.

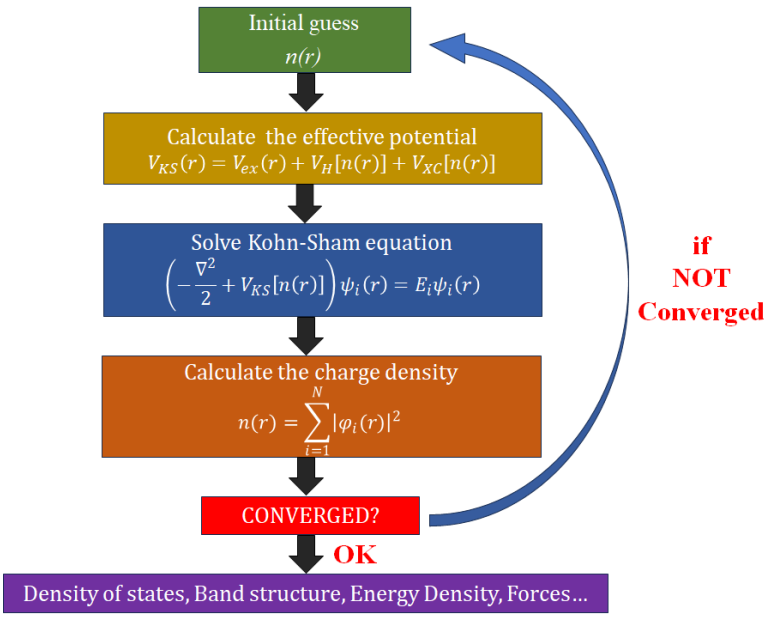

Figure 13: The self-consistent iterative cycle performed in density functional theory.

2.1.3 Exchange-correlation potential

The unknown part of KS equation is exchange correlation potential $V_{XC}[n(r)]$, as given in Eq. 7 (Burke and Wagner, 2013).

$$V_{XC}[n(r)] = \frac{\partial E_{XC}[\rho]}{\partial \rho(r)} \quad \text{Eq. 7}$$

There are many approximations designed for V_{XC} offering a competitive balance between accuracy and computational cost. The simplest one is local density approximation (LDA) for which the energy functional depends on local electron density as given in Eq. 8 (Perdew et al., 2005).

$$E_{XC}^{LDA}[n(r)] = \int E_{XC}(n) n(r) d^3 r \quad \text{Eq. 8}$$

The LDA approximation splits the exchange and correlation part with an assumption of having homogenous density all where, but this causes an error due to underestimating exchange and overestimating correlation energies. This inaccurate compensation of exchange and correlation parts lead to consider real inhomogeneous electron density in terms of its gradient. This improved Functional is referred to as generalized gradient approximation (GGA) given in Eq. 9 (Perdew et al., 1992).

$$E_{XC}^{GGA}[n_\uparrow, n_\downarrow] = \int E_{XC}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) n(r) d^3 r \quad \text{Eq. 9}$$

2.2 Data Collection

The DFT-based licensed packages of Wien2k (Kojima et al., 2009) and VASP (Bati et al., 2023) are available in the UAEU-HPC system, which were used to perform all computational works. VASP and wein2K use the periodic boundary conditions and pseudopotential method with the plane wave basis set. According to the periodic boundary conditions, the molecular wavefunctions should become zero at the infinite spatial coordinates and molecule is placed alone in unit cell of comparatively very higher dimensions.

2.2.1 Input Files

1. INCAR

It is the main input file for VASP code as shown in Figure 14, which defines the algorithms and parameters used in calculations. The main input tags mentioned in table 1 set the convergence conditions for ionic and electronic relations. After getting a relaxed structure, the INCAR-tags are changed for calculating further properties as shown in Figure 15 and 16.

Table 1: The list and description of important INCAR tags used in calculations.

INCAR Tags	**Description**
ENCUT	Sets the cutoff energy for convergence
NSW	Sets the maximum number of electronic steps to prevent non-converged calculations up on going forever
EDIFF	Defines breakdown condition for electronic relaxation self-consistent loop
EDIFFG	Defines breakdown condition for ionic relaxation self-consistent loop
ISIF	Describe which degrees of freedom are variable (position, cell volume/shape)
IBRION	Defines which algorithm is used for ionic relaxations

```
ISTART = 0              (Starts a new calc, ignoring any CHG or WAVE files left lying around)

#Parallel Options
 LPLANE = .TRUE.        (Real space distribution, true reccomended for linux cluster)
 NCORE =  5
 ISYM   = 2             (Set to 2 because system is non-centrosymetric)
 IALGO  = 48            (Algorithm, suggested 48 for large systems)

#Electronic Relaxation
 PREC     = Accurate    (Precision level for FFT grid)
 LREAL    = Auto        (Projection operators: automatic)
                        !VASP Manual: We recommend to use the real-space projection
                        !scheme for systems containing more than 20 atoms.)
 ENMAX    = 520.00 eV   (Plane-wave cutoff, set to largest ENMAX in POTCAR * 1.3 for relaxation)
                        !In this case, 400eV was the largest.
 NELM     = 100         (Max number of SCF steps)
 NELMIN   = 5           (Min number of SCF steps)
 GGA      =  PE         (PBE)
 EDIFF = 3E-08          (EDIFF = Same as in Gebhardt 2017)

#Relaxation
 IBRION=  2             (Relaxation algorithm)
 ISIF = 4               (For 2D, this relaxes, but fixes volume, to stop z vacuum collapsing)
 LVDW=.TRUE.            (Turns on van-der Waals forces)
 NSW = 800              (Tries x loops before repeating in the .sh)
 EDIFFG = -1E-02        (Force convergence in eV/A)

#Smearing               (For semiconductors or insulators, use the tetrahedron method (ISMEAR=-5),
                        !if the cell is too large (or if you use only a single or two k-points) use
                        !ISMEAR=0  in combination with a small SIGMA=0.03-0.05.)
ISMEAR = 0
SIGMA = 0.05
```

Figure 14: INCAR file for structure relaxation with all used tags and their set parameters with brief description in brackets.

```
ISTART = 1              (Starts a new calc, ignoring any CHG or WAVE files left lying around)
ICHARG = 11
#Parallel Options
 LPLANE = .TRUE.        (Real space distribution, true reccomended for linux cluster)
 NCORE =  2
 ISYM   = 2             (Set to 2 because system is non-centrosymetric)
 IALGO  = 48            (Algorithm, suggested 48 for large systems)
 ALGO   = Normal
#Electronic Relaxation
 PREC     = Accurate    (Precision level for FFT grid)
 LREAL    = Auto        (Projection operators: automatic)
                        !VASP Manual: We recommend to use the real-space projection
                        !scheme for systems containing more than 20 atoms.)
 ENMAX    = 520.00 eV   (Plane-wave cutoff, set to largest ENMAX in POTCAR * 1.3 for relaxation)
                        !In this case, 400eV was the largest.
 NELM     = 200         (Max number of SCF steps)
 NELMIN   = 5           (Min number of SCF steps)
 GGA      =  PE         (PBE)
 EDIFF = 3E-08          (EDIFF = Same as in Gebhardt 2017)
#Output files
 LORBIT  =   11
 NEDOS   =   1001
#Smearing               (For semiconductors or insulators, use the tetrahedron method (ISMEAR=-5),
                        !if the cell is too large (or if you use only a single or two k-points) use
                        !ISMEAR=0  in combination with a small SIGMA=0.03-0.05.)
ISMEAR = -5
SIGMA = 0.05
#Static Calculations
NSW  =  0
IBRION =  -1
LWAVE =  .FALSE.
LCHARG = .TRUE.
```

Figure 15: INCAR file used to calculate the density of states plots after performing single point calculation.

```
Elastic constants Calculation
IBRION    =  6         (Determine the Hessian matrix)
NFREE     =  2         (How many displacements are used for each direction, 2-4)
ISIF      =  3         (Stress/relaxation: 3-Shape/Ions/V)
NSW       =  1         (Max ionic steps)
PREC      =  High      (High level)
```

Figure 16: INCAR tags are used specifically to perform Mechanical calculation using Hessian matrix.

2. POSCAR

The second mandatory input file to run VASP calculations is POSCAR (as shown in Figure 17), which contains complete information about structure in term of ionic positions, lattice constants, and categories of elements, and number of each element in the formation of that specific configuration.

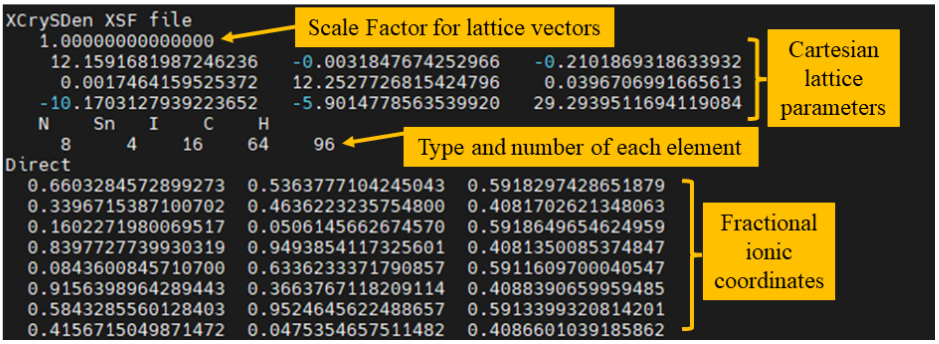

Figure 17: The POSCAR file displays the lattice parameters, types and number of elements, and positions of all atoms.

3. POTCAR

The POTCAR file consists of the pseudopotential for each element in the main structure, as shown in Figure 18. For more than one element, the POTCARs for all elements are concatenated in one POTCAR file, where the order of elements should be the same as set in the POSCAR file. VASP has a library of projected augmented wave-based pseudopotentials for all elements (Kresse & Joubert, 1999). Figure15 shows that the projected augmented plane wave potential with PE (Perdew-Ernzerhof) pseudopotential is used (Blöchl, 1994). For example, Br atom has seven valence electrons (ZVAL = 7.0) with the valence configuration of [s^2p^5]. The pseudopotentials are used to exclude core electrons by treating them as inactive core electron density.

```
PAW_PBE Br 06Jan2023
7.00000000000000000
Parameters from PSCTR are:
VRHFIN =Br: s2p5
LEXCH  = PE
EATOM  =   368.2131 eV,   27.0629 Ry
TITEL  = PAW_PBE Br 06Jan2023
LULTRA =        F    use ultrasoft PP
IUNSCR =        1    unscreen: 0-lin 1-nonlin 2-no
RPACOR =    1.900    partial core radius
POMASS =   79.904; ZVAL   =    7.000    mass and valence
```

Figure 18: The POTCAR file used for defining pseudopotentials for VASP calculations.

4. KPOINTS

The fourth input file for VASP calculations is KPOINTS, which specifies the k points (Bloch vectors) of the considered Brillouin zone (see Figure 19). A k-mesh is designed by subdividing the lattice vectors into the numbers being inversely proportional to dimensions of unit cell along x, y, and z axis. In the study of two-dimensional monolayer perovskites, the unit cell is extended along z-axis leading to k-point mesh of 4×4×1 dimensions.

```
Regular k-points mesh generation
0                ! 0 = determines number of k points automatically)
M                ! (Generates Monkhorst pack mesh)
4    4    1      ! (Subdivisions N1, N2n N3 along reciprocal lattice vectors
0.0  0.0  0.0    ! (Optional shift of mesh)
```

Figure 19: KPOINTS file used for relaxation and post processed calculations.

2.2.2 Output Files

The CONTCAR file (sharing the same scheme of POSCAR) has the position coordinates of the relaxed structure, which can be visualized by using XcrysDen and Vesta. To display the output data in plots, Origin and Python codes were used. The main output files include:

1. CONTCAR: Contains the atomic coordinates of the relaxed structure.
2. OSZICAR: Contains data of electronic and ionic steps.
3. OUTCAR: Contains the complete information about the performed calculation.
4. CHGCAR: Contains the charge density of the relaxed system.

5. DOSCAR: Contains the partial and total density of states.

Novel Half-Heuslers and Perovskites will be investigated through calculating their structural, mechanical, electronic, thermodynamic, thermoelectrical properties, power factor and photovoltaic efficiency. By introducing the partial defects, the whole chemical scheming will be altered, thus offering a new material with diverse photovoltaic properties. The desirable material should be more efficient, less toxic, more stable, and cost effective (Javed et al., 2022b, 2020; Sattar et al., 2023).

2.3 Results and Discussions

In this sub-section, we have comprehensively discussed the main results and findings obtained under this project.

2.3.1 Article I

A DFT-based study of structure and electronic scheming of undoped (pure) and doped $(R\text{-}NH_3)_2Pb_{1-x}Ge_xI_4$configurations was presented using spin-orbit coupling. Depending on the organic-spacer-cations $[R\text{-}NH_3]^+$ of methyl-ammonium ($CH_3NH_3^+$) and Phenyl-ethyl-ammonium ($C_6H_5[CH_2]_2NH_3^+$),varied compositions of Ge cation in replacement of Pb cation at varying concentration of x (0.0, 0.25, 0.50, 0.75, 1.0), 32-configurations were designed. Depending on location of Ge dopant, we got four permutations for 25% Ge, six permutations for 50% Ge (four Columns & two Battenberg), and four permutations for 75% Ge, as shown in Figure 8. An intriguing interplay between the structural distortion and angular tilting is discovered, which leads to the bandgap bowing for mixed Pb-Ge compositions (Javed et al., 2022a).

2.3.2 Article II

We also analyzed the effect of different spacer cations $[R\text{–}NH_3]^+$on the conjunction with different inorganic halide anions by introducing a novel class of 2D-perovskites. A larger spacer cation was found to reduce the band gap. Interesting features of dielectric confinement, quantum confinement, defect tolerance, low effective masses, and high mobility were explored by understanding a relationship between the compositional and electronic variations (Javed et al., 2023a).

2.3.3 Article III

We also investigated the effect of the biaxial strain on novel 2D-perovskites and found that the band gap decreases under compression and increases under elongation. Formation of PH_I trap states in CBM and I_i trap states in VBM under tensile and compressive strains are responsible for bandgap alterations, thus a significant impact on electronic properties opened the exciting possibilities for controlling and manipulating their optoelectronic devices (Javed et al., 2023b).

2.3.4 Article IV

We have designed a novel Half-Heusler CrMnS alloy and investigated its structural, elastic, magnetic, thermodynamic, and thermoelectric properties. The alloy was found to be chemically, thermodynamically, and vibrationally stable with an optimized lattice parameter 5.49 Å at -92.4 eV. Cohesive and formation energy analysis, along with the phonon dispersion curve, also supported this stability. The CrMnS hold half-metallic nature with their spin-up and spin-down channels showing metallic and semiconductor nature as found from spin-polarized band structures and density of states plots. Slater Pauling rule also satisfy the 100% polarization with 1 μ_B magnetization. CrMnS serves as a potential candidate for thermoelectric and spintronic applications with ZT curve approaching 0.72 value at 600K temperature (Javed et al., 2022b).

2.3.5 Article V

A novel series of Cr-based Half-Heuslers alloys CrVZ was investigated with three p-block chalcogenides including S, Se, and Te. The electronic studies found all structures are half-metallic with CrVSe exhibiting direct bandgap of 1.07 eV for spin-up states. CrVSe and CrVTe structures were found structurally, thermodynamically, and vibrationally stable except CrVS with presence of soft imaginary phonon due to smaller sized S-ion. Interestingly CrVS and CrVTe were found to have similar indirect bandgap of 1.14 eV for spin-up states. But the thermoelectric performance of CrVTe is found extremely higher as compared to S- and Se-based alloys. Te-based alloys with the largest Seebeck co-efficient and highest power factor proved to be a promising choice for thermoelectric applications (Javed et al., 2020).

Chapter 3: Conclusion and Future Perspectives

An organized investigation on the structure, property, performance, and processing establishes an important paradigm in material sciences. To achieve the sustainability development goals (SDGs) by 2030, the renewable energy-based devices are required to be explored, improved, and commercialized, so as to introduce a green environment. To meet the ever-increasing worldwide electricity demand through reducing air-polluting carboneous fuels consumptions with industrial waste-heat emissions, there is a direct need to launch photo-converted and thermoelectric modes of electricity generation. In this regard, two energy harvesting materials (perovskites and half-heuslers) have become one of the research hotspots.

3.1 Photovoltaic Implications

To evaluate the photovoltaic performance of perovskites absorber, a deep theoretical investigation of crystal structure, optoelectronic behavior and mechanical stability is required. In this work, the role of defect engineering (by doping A, B, and X ions) and strain engineering is analyzed and studied theoretically with the main conclusive explanations of bandgap tunning, octahedral distortion, octahedral tilting, energy level alignments, spin-orbit coupling effect, quantum and dielectric confinement, and defect tolerance.

3.2 Thermoelectric Implications

Half-heuslers alloys with excellent thermodynamic, mechanical, vibrational stabilities and promising thermoelectric features have emerged as an ideal candidate for economically designing the viable, energy efficient and environmentally friendly devices. In this work, CrMnS, CrVS, CrVSe, CrVTe, VCrTe, VFeTe, and VCoTe were investigated. Besides, anti-perovskites A_3OX (A = K, Na, Li and X = Br, I, Cl) were also found to be breakthrough thermoelectric candidates. Also, the electronic, elastic, structural, magnetic, thermodynamic, vibrational, and thermoelectric properties of these materials were calculated. Designing novel HH alloys through defect engineering is found to remarkably enhance the thermoelectric performance of these materials. Our findings pave the way to implement these innovative HH alloys in the pursuit of real-world TE and spintronic applications.

3.3 Future Prospectives

In the pursuit of scientific progress and sustainability, the primary objective of this project is to significantly contribute towards the goals of sustainable development by launching the improved, cost-effective, stable, and convenient energy harvesting materials. The efficient perovskites and promising thermoelectric half-heuslers alloys can be further harnessed with the potential of machine learning, which can train a model feature and engineer the components focused on calculated bandgaps. It empowers us to conduct the robust research for even more efficient materials. The experimental synthesis of these innovative materials will actualize the long-term goal of natural energy harvest facilitated with mass production of cutting-edge technologies, fostering the global economy and industrialization.

The overarching grand goal of this thesis is to delve deep into a comprehensive understanding of the electronic, structural, and optical properties of the investigated perovskite and half-Heusler materials. A thorough understanding and knowledge of all these properties can facilitate designing and optimize energy harvesting devices based on these materials. The results of this thesis hold immense potential for developing the next-generation energy harvesting technologies, propelling us closer to the grand ambition of achieving sustainable and clean energy for all. Thus, an awe-inspiring fusion of scientific exploration, sustainability, and technological innovation can play a pivotal role in the pursuit of a greener future.

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List of Other Publications

I. Sattar, M.A., Javed, M., Al Bouzieh, N., Benkraouda, M., Amrane, N., (2023). First-principles investigation on the novel half-Heusler VXTe (X= Cr, Mn, Fe, and Co) alloys for spintronic and thermoelectric applications. Materials Science in Semiconductor Processing, 155, 107233. https://doi.org/10.1016/j.mssp.2022.107233

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UAE UNIVERSITY DOCTORATE DISSERTATION NO. 2023: 43

Density Functional Theory based computational study of innovative energy harvesting materials: Half-Heuslers and Perovskites class is presented with deep understanding and investigation of their structural, electronic, magnetic, optical, mechanical, thermoelectric, and thermodynamic properties under defect and strain engineering highlighting their role as promising next-generation photovoltaic and thermoelectric contenders with a structure-characteristics-property-processing-performance relationship.

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