DOI: 10.36868/ejmse.2025.10.02.077

COMPUTATIONAL INVESTIGATIONS INTO THE PHYSICAL PROPERTIES OF CHALCOGENIDE PEROVSKITES MgBS₃ (B = Hf, Ti, and Zr) FOR PHOTOVOLTAIC APPLICATIONS: DFT INSIGHT

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Abstract

A promising class of materials, chalcogenide perovskites (CPs), are characterized by their exceptional stability, environmentally friendly composition, and intriguing optoelectronic properties. To comprehensively analyze the structural, mechanical, and thermodynamic characteristics of $MgBS_3$ (where B = Hf, Ti, and Zr), one of the most promising members of the metal chalcogenide perovskite family, we employed density functional theory (DFT) simulations. Our theoretical results indicate that $MgHfS_3$ is the most stable compound, aligning well with the reported syntheses of other chalcogenide perovskites. These materials exhibit anisotropy, robust mechanical stability, and significant resistance to deformation under external stress, fulfilling the Born stability criteria. Pugh ratio analysis confirms that MgZrS₃ (1.99) is ductile, as well as MgHfS₃ (1.91) while MgTiS₃ (0.05) is brittle. Thermodynamic calculations reveal the Debye temperatures of MgHfS₃ (282.94 K), MgZrS₃ (325.67 K), and MgTiS₃ (376.76 K), along with vibrational energies, entropies, and constant volume heat capacities of MgHfS₃ (115 JK⁻¹Nmol⁻¹) and $MgZrS_3$ (112 JK⁻¹Nmol⁻¹). Notably, the free vibrational energy decreases rapidly with increasing temperature. These characteristics underscore the potential of MgBS₃-based CPs in developing more robust and efficient optoelectronic devices and indoor photovoltaics. Furthermore, due to its lower Debve temperature compared to other CPs, MgHfS₃ emerges as a significant candidate for thermodynamic applications. Our findings suggest that MgBS₃ chalcogenide perovskites (B = Hf, Ti, and Zr) possess substantial promise for advancing ferromagnetic materials, renewable energy solutions, and optoelectronic devices.

Keywords: Chalcogenide-perovskites, mechanical, structural, thermal, photovoltaic and optoelectronics.

Introduction

The global energy landscape is currently moving toward sustainable and renewable energy sources to lower greenhouse gas emissions and lessen the effects of climate change. Scientific communities throughout the world have been investigating new materials that may help create a more sustainable, highly productive, and long-lasting future to solve these issues [1-3]. Perovskites, skutterudite, metal-organic frameworks, covalent organic frameworks, metal chalcogenides, and intermetallic have all been identified as having the capacity to provide alternative energy. Metal chalcogenides, which are composed of elements from the chalcogen group (oxygen, sulfur, selenium, and tellurium), have attracted interest among these materials due to their varied characteristics. Chalcogenide nanomaterials have their roots in the early research on amorphous chalcogenide semiconductors (Figure 1a) conducted in the 1960s. The unique combination of optical, electrical, thermal, and catalytic properties of chalcogenide

semiconductor nanoparticles makes them ideal for a variety of uses in environmentally friendly nanotechnology and remediation (Figure 1) [4, 5].

Chalcogenide perovskites represent a promising class of materials that aim to integrate the advantageous application-specific characteristics of both halide perovskites and chalcogenides. A particularly noteworthy application is their potential use in tandem solar cells built on silicon platforms. While halide perovskites demonstrate high efficiency, they suffer from limited longterm stability and the presence of toxic elements [6-10]. Conversely, established chalcogenide alternatives, including CdSe, CdTe, Cu(In,Ga)(S,Se)₂, and Cu₂ZnSn(S,Se)₄, are recognized for their stability [9]. However, they tend to experience significant voltage losses relative to the Shockley-Queisser limit when their band gaps are adjusted to the optimal range for tandem cells, approximately 1.6 to 1.8 eV [11-14]. Other emerging wide-gap chalcogenides show limited evidence of high photovoltaic potential, particularly in terms of strong luminescence quantum yield. In contrast, chalcogenide perovskites overcome the drawbacks associated with both material groups. They primarily consist of earth-abundant and non-toxic elements, demonstrating exceptional environmental stability [15-17]. Furthermore, they possess higher absorption coefficients than any mainstream chalcogenide or halide perovskite, with some exhibiting external luminescence efficiencies that theoretically enable a V_{oc} reaching 90% of the Shockley-Queisser limit. These attributes are promising for the application of chalcogenide perovskites as the top cell in tandem solar cells, as well as in other energy conversion applications, including solid-state lighting [18-20]. In terms of the discovered (or predicted) chalcogenide perovskites, it is evident that this family is less extensive than many authors have previously imagined [21].



Fig. 1. Overview of the chalcogenide's energy and environmental applications

Despite some conflicting claims, the prevailing understanding is that all practically applicable II-IV-VI₃-type ABX₃ compounds are sulfides, with BaZrS₃ and BaHfS₃ definitively exhibiting a ground state perovskite structure. Other compounds, such as the Sr-equivalents, may form as high-temperature phases [22-25]. Several III-III-VI₃-type ABX₃ perovskites have been demonstrated, but their exploration has been limited to basic structural parameters thus far. The relative scarcity of chalcogenide perovskites can be attributed to nonideal structural factors, particularly the lack of sufficiently large B-site cations necessary to meet the minimum octahedral factor requirement [26]. Nevertheless, there is considerable potential for tuning bandgap and other properties through alloying at any of the lattice sites of BaZrS₃, while high-temperature phases may still be applicable in areas such as solid-state lighting [27]. These observations clarify the limited number of publications on chalcogenide perovskites beyond BaZrS₃, allowing us to concentrate our efforts on this more restricted family of materials for which more information is accessible. There are several gaps and uncertainties in the existing literature regarding structural stability and characterization, which we have identified [28-32]. The incorporation of chalcogenides, including selenium and sulphur, offers a significant opportunity to improve the efficiency and stability of perovskite solar cells (PSCs). Nevertheless, this integration poses several challenges. Primarily, the comparatively higher cost of these materials relative to alternatives utilized in PSCs may result in elevated manufacturing expenses, thereby requiring meticulous optimization to avoid substantial increases in production costs. To improve structural stability, Md. Zillur Rahman *et al.* (2024) introduced new CP materials featuring adequately large B-site cations that meet the minimum octahedral factor requirement, along with their characterization [33].

The existing literature, primarily based on powder samples, demonstrates the favourable optoelectronic properties of chalcogenide perovskites [34]. These powder materials have confirmed exceptionally strong optical absorption; however, there is a notable lack of consensus regarding the size and nature of the bandgap, particularly in BaZrS₃. In terms of photoluminescence (PL) emission, the high-temperature phases SrZrS₃ and SrHfS₃ have shown superior results compared to BaZrS₃[35-36]. Nevertheless, the limited data points raise questions about whether this indicates an intrinsic difference, and the influence of impurities and secondary phases remains unclear [37]. The PL broadening observed in BaZrS3 is concerning and warrants evaluation in better-characterized materials produced under more controlled conditions. Meanwhile, sensitive measurements of absorptivity will be crucial for understanding the potentially unusual band structure and the nature of any sub-gap states. Additionally, the reported high dielectric constant of BaZrS₃ holds significant technological promise, particularly for enhancing charge carrier lifetimes [38]. The distinctive combination of a Dirac-like band structure, elevated carrier mobility, and a three-dimensional framework in Ba2HfTe4 positions it as a highly promising material for diverse applications. In the realm of energy conversion, its superior carrier mobility has the potential to greatly enhance the efficiency of photovoltaic devices by facilitating improved charge transport. Additionally, in sensing technologies, the material's stability and electronic characteristics may pave the way for the creation of more sensitive and reliable sensors. Recently, Njema et al. (2024) conducted a review that outlines methods for enhancing charge carrier lifetimes and achieving a high dielectric constant in other conductive polymers, thereby advancing their technological potential [39].

In terms of defect tolerance, which is a cornerstone of the success of halide perovskites, the available information regarding chalcogenide perovskites remains limited. Consequently, a comprehensive comparison between halide and chalcogenide perovskites in this context is currently unfeasible. The two theoretical studies, albeit focused solely on BaZrS₃, suggest that BaZrS₃ exhibits defect tolerance, as it lacks low-energy defects with deep energy levels that could lead to Shockley-Read-Hall recombination [40-42]. This conclusion is further corroborated by existing photoluminescence (PL) measurements. Nevertheless, while the findings are promising, the information remains fragmented. More work is still needed to make a direct and detailed comparison of the defect chemistries at this stage, including on the roles of other defect types, including everpresent impurities such as O and Hf. Clearly, there is scope for material processing to impact defect concentrations, and several chalcogenide perovskites [43] have demonstrated the technologically useful feature of variable doping level and type. Reasonable charge carrier mobilities for emerging materials have been reported, especially promising to consider that most optoelectronic and transport measurements have been made on relatively poor-quality materials from high temperature synthesis, which is expected to lead to degenerate doping and large off stoichiometry. This suggests there is room for improvements in all characteristics thus far determined [44, 45]. G.G. Njema and J.K. Kibe (2025) have presented both theoretical and experimental findings that offer an alternative approach to enhancing the defect tolerance of conducting polymers (CPs). Their research focuses on optimizing doping levels, stoichiometry, and related factors to facilitate technological advancements in CP materials [46].

Thin film synthesis has emerged as a significant challenge for chalcogenide perovskites. The appropriate synthesis methods appear to be more like those used for other chalcogenides rather than for halide perovskites. While solution processing is often regarded as a competitive advantage of halide perovskites, it is likely not feasible for chalcogenide perovskites. This limitation is presumably due to the necessity for thermal activation of chemical rearrangements, which is influenced by the stronger chemical bonds present. However, these characteristics also contribute to the inherent stability of the materials. Although solution-processable materials facilitate rapid advancements in research and development, the requirement for high-temperature processing may ultimately result in enhanced stability. For instance, both CdTe and CIGS necessitate high-temperature processing yet do not face the significant stability challenges associated with halide perovskites. Furthermore, the primary obstacles for CdTe and CIGS technologies are unrelated to their high-temperature processing, and their embodied energy remains considerably lower than that of Si-based technologies, owing to their thin film characteristics [46. 47,48]. Synthesis efforts for chalcogenide perovskite thin films, specifically BaZrS₃, have predominantly utilized physical vapour deposition methods. A prevailing notion suggests that chalcogenide perovskites necessitate unusually high growth temperatures and are incompatible with conductive substrates, posing significant challenges for photovoltaic integration. However, our review of the literature indicates that this characterization may be premature [49]. Two primary bottlenecks are evident. The first is a notable issue of low diffusivity, which hinders phase formation and grain growth of BaZrS₃. The second challenge involves the difficulty of substituting oxygen with sulfur when employing oxide precursors, which has been the most common approach to date. Insights from the solid-state synthesis literature offer valuable guidance for thin film growers. One key takeaway is the complete avoidance of oxide precursors [50]. Additionally, a phase formation pathway through BaS₃ appears to exhibit much faster kinetics, enabling lower temperature growth that is comparable to other chalcogenides. This method should be straightforward to replicate in thin film growth, yet it has remained unreported thus far. The combination of these insights, along with the use of additives to enhance crystallization-already a standard practice for other chalcogenides, indicates significant potential for improving material quality through thin film techniques, surpassing the advancements achieved with bulk samples. Such enhancements are anticipated to foster a deeper understanding of the optoelectronic properties of emerging chalcogenide perovskites and facilitate progress toward device integration [51].

As a remedy, sustainable synthesis pathways and alternate chalcogen sources are being researched. We aim to support a renewed push for development of chalcogenide perovskites and to create clarity in the face of some early misconceptions and disappointing experimental outcomes that sit alongside various impressive claims, and to identify the critical hurdles that would need to be overcome for chalcogenide perovskites to emerge fully onto the PV stage. This has motivated us to perform a detailed study of the mechanical, thermodynamic, and structural characteristics of the MgBS₃ (B = Hf, Ti, and Zr) perovskite as a functional pressure using density functional theory-based first-principles calculations (DFT). Details of the lattice parameters under pressure are provided. In the meantime, the elastic constant and other mechanical parameters, such as elastic moduli, are also established. In Section 2, the computational details of the calculations are presented. Our results are in Section 3. An overview of the findings is provided in Section 4.

Computational Methodology

The exchange-correlation functional was described using the generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) [52] in first-principles calculations carried out with the Quantum Espresso algorithm [53]. (XC). For atoms having valence electrons in Hf, Zr, Ti, and S, the all-electron projector augmented wave (PAW) technique was used. of [Xe] $4f^{14} 5d^2 6s^2$, [Kr] $4d^2 5s^2$, [Ar] $3d^2 4s^2$, and [Ne] $3s^2 3p^4$, respectively. A plane wave set with an energy cut-off of 50 Ry served as the foundation for the expansion of the electronic wave functions' plane waves. The Monkhorst-Pack [54-55] $4 \times 4 \times 4$ k-point mesh was merged with the irreducible Brillouin zone. Every

structure was compressed between 0 and 15 GPa, and it was relaxed at each pressure point under investigation. To attain high pressures, the volume of the original existing structure was later decreased from ambient pressure. To maintain a balance between speed and precision, the plane-wave basis cutoff was set at 750 eV. The ionic cores and the valence electron interactions were described by an ultrasoft pseudo-potential [56]. The energy levels were widened using the Methfessel-Paxton [57] smearing with a Gaussian spreading $\sigma = 0.01$ Ry to enhance the convergence of the solution of the self-consistent Kohn-Sham equations. A well-converged ground state energy was obtained by setting the total energy convergence in the iterative solution of the Kohn-Sham equations [58,59] at 1.0×10^{-7} Ry. The BFGS algorithm [60] was utilized to fully relax all structures, using a threshold force of 10^{-3} Ry/Bohr.

Results and Discussions

Structural properties



Fig. 2. Predicted material structures of: a) MgHfS₃; b) MgTiS₃; c) MgZrS₃

Based on the output data presented in Figure 2., we observed that the materials exhibit an orthorhombic perovskite structure. The software XCRYSDEN was utilized to create the anticipated figures [60-61]. Table 1. illustrates the three-dimensional arrangement of the structure along with all essential properties of the perovskites. The results align closely with previous studies on both experimental and theoretical values of lattice constants. Figure 3. illustrates a parabolic curve generated by plotting the total energy of MgBS₃ against the lattice constants. The minimum energy values are 9.59Å for MgHfS₃, 9.27Å for MgTiS₃, and 9.19Å for MgZrS₃. In comparison to the k-point sample curve, this minimum exhibits the lowest total energy cut-off and demonstrates convergence, indicating it is the most favourable point for optimization, as analyzed in Figure 3.

Table 1. Table showing calculated GGA lattice constant a_0 (Å), b	b (°A), c(°A) bulk modulus B and Moduli derivative B ¹
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Crystals	Space group	a(°A)	b(°A)	c(°A)	B ⁰ (GPa)	\mathbf{B}^{I}	
MgHfS3,	Pnma	6.56	7.02	9.59	78.9	5.57	
MgZrS3	Pnma	6.56	7.03	9.19	251.3	6.01	
MgTiS ₃	Pnma	6.66	7.03	9.27	170.6	4.43	
BaZrS3-β*	Pnma	7.02	7.05	9.98	-	-	
BaZrS3-a*	Pnma	7.04	7.15	10.03	-	-	

* Ref 40



Fig 3. Energy-Volume relationship for: a) MgHfS₃; b) MgZrS₃; c) MgTiS₃

Table 2. The calculated GGA lattice constant a_0 (Å), bulk modulus B, equilibrium volume V_0 (Å³) and band gap E_g forMgTiS₃, MgHfS₃ and MgZrS₃ compared to other theoretical studies and experiment

Physical parameter	MgTiS ₃	MgZrS ₃	MgHfS ₃	Theory	Experiment
Lattice constant a ₀ (Å)	9.27	9.19	9.59	10.077[39]	9.98[40]
Bulk modulus B (GPa)	251.3	170.6	78.9	-	-
Volume V ₀ (Å ³)	117.06	424.09	439.53	511.059[38]	441.89 [40]
Band gap Eg (eV)	1.1	1.3	1.43	0.9-1.6[40],1.0- 1.75[36],1.12[37	1.73-1.85[38],] 0.99[38]
Emin (Ry)	-517.07	-2125.22	-2470.2	-	-
Tolerance factor	0.79	0.75	0.76	-	-

A well-established principle regarding the stability of materials is that it is closely linked to their formation energy. Generally, a more stable material is characterized by lower formation energy, while for thermal stability, the formation energy must be negative. The calculated volume parameters for the materials are as follows: 117.06 Å for MgTiS₃, 439.53 Å for MgHfS₃, and 424.04 Å for MgZrS₃, as illustrated in Table 5. and Fig. 3. The method of approximation employed significantly influences the compound's volume, leading to discrepancies when compared to other studies [62]. Additionally, the choice of pseudopotential is crucial for enhancing structural properties [63-65]. The structural parameters obtained were utilized to compute various other physical properties of the materials. Further details derived from the Murnaghan equation of state are provided in Table 2.

Evidence regarding elastic characteristics provides crucial details about the mechanical strength of materials, encompassing moduli and Poisson's ratio. The strength of each crystal structure is determined by its mechanical stability criteria, which for orthorhombic crystals are outlined in references [66]. When evaluating the hardness of approach line materials, the most significant elastic parameters include the bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (n). Utilizing the values of these moduli, the following relationships are established based on the computed data, as presented in Table 3. This knowledge encompasses the moduli and Poisson's ratio (v). The strength of every crystal structure is a function of its mechanical stability criteria, with the stability criteria for orthorhombic crystals detailed in references [67].

The bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (n) represent key elastic properties for line materials when assessing their hardness. Utilizing these moduli, calculations can be performed based on the computed data, as outlined in the relations provided in references [64-67] and summarized in Table 3.

$$C_{11} + C_{22} - 2C_{12} > 0, C_{11} + C_{33} - 2C_{13} > 0$$
⁽¹⁾

$$C_{22} + C_{33} - 2C_{23} > 0 \tag{2}$$

$$C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23} > 0$$
(3)

$$C_{11} > 0, C_{22} > 0, C_{33} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0$$
⁽⁴⁾

The equations 1 to 4 are utilized to determine the nine elastic constants of the orthorhombic structure of the materials under investigation, employing the strain-stress method derived from Hooke's law [68]. Following the calculation of the elastic constants for MgHfS₃, MgZrS₃, and MgTiS₃, as presented in Table 3, we subsequently applied the relationships outlined in equations (4) to (10) to derive the elastic constants from Table 3, resulting in the findings illustrated in Tables 4. and 5. Our analysis of Table 3 indicates that the values of the elastic constants align with the stability criteria, suggesting that the materials exhibit mechanical stability. The hierarchy of stability among the materials is as follows: MgHfS₃ > MgZrS₃ > MgTiS₃. The limited stability of MgTiS₃ can be attributed to the negative values of C₁₁, C₂₂, and C₃₃, leading to the conclusion that this material is mechanically semi-stable at temperatures below 300K, but lacks stability at elevated temperatures. Due to the polycrystalline nature of the materials in technological characterization, it is imperative to calculate the moduli of bulk B and shear G from their elastic values using relations (5) and (6). The B and G are being calculated within the Voigt-Reuss-Hill (VRH) approximation [69-70]. The calculated approach for bulk and shear modulus is according to these formulations.

$$B = \frac{1}{2}(B_V + B_R) \tag{5}$$

$$G = \frac{1}{2}(G_V + G_R) \tag{6}$$

where subscript V = Voigt bound, subscript R = Reuss bound.

The comprehensive analysis of the mechanical properties, specifically the moduli of E, G, and B, for the materials MgHfS₃, MgZrS₃, and MgTiS₃ is presented in Table 4. The bulk modulus B is recorded as 51.58 GPa for MgHfS₃, 51.56 GPa for MgZrS₃, and 5.78 GPa for MgTiS₃. These findings are in closer alignment with the theoretical values of 69.9 GPa for the GdFeO₃-type and 75 GPa for another distorted theoretical result [37-40]. The bulk modulus serves as an indicator of the materials' compressibility under hydrostatic pressure, with higher values signifying greater compressibility. The shape of the material is influenced by the area shear modulus, where a higher value indicates increased resistance to dislocation. Notably, MgTiS₃ exhibits the lowest resistance to dislocation, as detailed in Table 4. Additionally, the Young's modulus reflects the hardness of the solids; as illustrated in Table 4., the hafnium and zirconium chalcogenides display similar hardness values, while titanium demonstrates the least hardness among the materials analyzed.

Crystals	C11	C22	C33	C44	C55	C66	C12	C13	C23
MgHfS ₃	1213.65	1238.9	1207.2	169.44	159.68	155.71	152.76	164.84	193.4
MgTiS ₃	-69.66	-131.58	-133.58	179.76	188.13	185.77	110.82	134.11	160.1
MgZrS ₃	1275.7	1224.1	1231.7	143.6	149.56	153.24	158.51	144.11	165.7

Table 3. Table showing calculated elastic constants of MgHfS₃, MgTiS₃ and MgZrS₃

The investigation into the brittleness and ductility of the materials was conducted using the Pugh ratio (B/G) [71]. The calculated B/G values of ≥ 1.75 for MgHfS₃ and MgZrS₃ indicate ductility, while the titanium counterpart is classified as a brittle material. Further analysis of the ductile and brittle characteristics was performed through Cauchy pressure calculations, as expressed in the relation (Cp = C₁₂–C₄₄), detailed in Table 5. The Zener anisotropic factor (A) quantifies the degree of elastic anisotropy in materials [72]. An anisotropy factor of 1 signifies an isotropic nature, whereas values deviating from this indicate varying degrees of elastic anisotropy; specifically, materials with A greater than 1 are highly anisotropic, while those with A less than 1 exhibit lower anisotropy [73]. Our findings reveal that the materials are indeed anisotropic, as illustrated in Table 5. This characteristic suggests a potential for crack initiation during crystal growth [74]. Finally, we assessed the bonding characteristics of the materials through Poisson ratio estimations, which fall within the range of 0.25 to 0.42, as shown in Table 5. The data indicates metallic bonding for MgHfS₃ and MgZrS₃, while MgTiS₃ is associated with non-metallic bonding.

In confirming their stability, Born's mechanical stability criteria was adapted.

$$C_{22} + C_{33} - 2C_{23} > 0 \tag{7}$$

$$C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23} > 0$$
(8)

The mechanical stability of the three materials is ranked as follows: MgHfS₃ exhibits the highest stability, followed by MgZrS₃, with MgTiS₃ demonstrating the least stability. A comparison of our MgZrS₃ with the findings in reference [75] revealed similarities in the elastic constants when subjected to pressures ranging from 2 to 8 GPa. The observed discontinuities between 6 and 8 GPa can be attributed to a reduction in bond length due to increased compression; however, the material effectively accommodates higher pressure effects, stabilizing between 8 and 18 GPa, which corresponds with a thermodynamic increase in temperature from 300K to 800K. Structural analysis, conducted using the Birch-Murnaghan equation of state, also yielded comparable values. Discrepancies noted between our findings and those in the cited paper may stem from the extended potential of HSE06 employed to fine-tune the peaks and results. Additionally, the results obtained using the exchange-correlation GGA approximation aligned with our findings and those of reference [76], as well as other selected chalcogenide perovskites listed in the table. Furthermore, the influence of spin-orbit coupling and the SOC formulation utilized in the paper may also contribute to the observed discrepancies in results.

Figure 4.0 illustrates the dynamic stability of the three chalcogenide perovskites. Despite being subjected to varying angles and pressure levels, these materials demonstrate a degree of stability within the range of 0 to 20 GPa. Our study indicates that the lattice characteristics of the materials diminish as hydrostatic pressure increases, reinforcing the notion that a material's strength declines with heightened supplemental pressure. The results reveal that MgHfS₃ exhibits greater pressure stability compared to MgZrS₃ and MgTiS₃, with MgTiS₃ showing the least strength under stress, as depicted in Figures 4.a. and 4.b. In Figure 4, the comparison of unit cells under pressure yielded results consistent with previous findings, maintaining the same trend as pressure escalated. Meanwhile, Figure 5. demonstrates that MgHfS₃, at an elastic constant of 200 GPa, achieves a maximum pressure stability of 8-10 GPa. In contrast, MgZrS₃, with an elastic constant

of 1200 GPa, can endure pressure influences ranging from 8 to 15 GPa, while MgTiS₃, at an elastic constant of 1100 GPa, withstands pressure stability between 8 and 13 GPa.



Fig. 4. Lattice parameters variation with pressure for: a) MgHfS₃; b)MgTiS₃; c) MgZrS₃



Fig. 5. Elastic constants variation with pressure for: a)MgHfS₃; b)MgZrS₃; c)MgTiS₃

Thermal properties

Two primary parameters influence the thermal properties of a solid: melting temperature (M_t) and Debye temperature (θ_D) . The elastic constants, melting temperature, and specific heat capacity are all contingent upon the Debye temperature, as referenced in [77]. Additionally, the sound velocities—mean, longitudinal, and transverse—calculated through the Debye temperature, are presented in Table 4.

$$\Theta_D = \frac{h}{\kappa_B} \left(\frac{3_n}{4\pi V_a}\right)^{\frac{1}{3}} V_m \tag{9}$$

where V_m = average sound velocity, k_B = Boltzmann's constant value, h = Planck's constant value, n = number of atoms/molecules, N_A = Avogadro's number. The sound average velocity V_m can be obtained by [55]

$$V_M = \left[\frac{1}{3} \left(\frac{1}{V_L^3} + \frac{2}{V_L^3}\right)\right]^{\frac{-1}{3}}$$
(10)

$$V_l = \sqrt{\frac{3B + 4G}{3\rho}} \tag{11}$$

The calculated Debye temperatures for MgHfS₃, MgZrS₃, and MgTiS₃, along with their stability, are detailed in Table 5. Previous studies, including those on BaZrS₃, indicate that the Debye temperature of materials correlates with thermal conductivity; specifically, higher temperatures are associated with increased thermal conductivity [78,79]. As shown in Table 4., the Debye temperatures of the materials are ranked as follows: $MgHfS_3 < MgZrS_3 < MgTiS_3$. Notably, MgTiS₃ exhibits the highest Debye temperature, which is related to its larger density, consequently resulting in superior conductivity. Given that the Debye temperature is influenced by the strength of chemical bonds, a higher Debye temperature in any compound suggests stronger chemical bonding. Specifically, MgHfS₃ has the lowest Debye temperature at 282.94 K, while MgTiS₃ has the highest at 376.76 K, indicating that MgTiS₃ possesses better chemical bonds compared to the other two materials. Additionally, the melting temperature of a material is proportional to its Debye temperature [80], a relationship that holds true for the materials listed in Table 4. However, to the best of our knowledge, there are no existing reports on the theoretical and experimental investigations of the melting and Debye temperatures for MgHfS₃, MgZrS₃, and MgTiS₃. Literature comparisons between other chalcogenides and selected Heusler alloys are available [81-83]. Therefore, our theoretical findings on melting and Debye temperatures could serve as a valuable reference for future research.

Material	В	G (GPa)	B/G	E (GPa)	ρ	$\theta_{\rm D}$	Vm	Mt
	(GPa)				(g/cm ³)	(K)	(m/s)	(K)
MgHfS ₃	51.58	27.04	1.91	68.85	3.9451	282.94	2717.57	802.567
MgZrS ₃	51.56	25.81	1.99	66.08	2.7936	325.67	3138.46	839.239
MgTiS ₃	5.78	109.05	0.05	33.58	2.2215	376.76	-	441.29
BaZrS ₃ **	69.9	33.5	2.09	86.6	4.269	315.9	-	1179
CaTiO ₃ *	72.1	38.6	1.87	98.2	4.209	337.6	-	1409

Table 4. Table showing bulk modulus B(GPa), shear modulus G(GPa), Young Modulus E(GPa), Pugh ratio B/G,density ρ (g/cm³), Debye temp θ_D (K) with average speed of sound v_m (m/s) and melting point M_t (K) thru Voigt-Reuss-Hill approximation for MgHfS3, MgTiS3 and MgZrS3

** ref 62 * ref 61

 Table 5. Table showing calculated Cauchy pressure, C'(GPa), Anisotropy nature of the materials and Born's Mechanical stability criteria

Crystals	С'	Α	BM	Poisson
MgHfS ₃	1044.22	0.31942	Stable	0.27805
MgZrS ₃	1132	0.2569	Stable	0.28024
MgTiS ₃	-249.24	-1.992	Unstable	-0.89993
BaZrS3 **	-	0.330	Stable	-
CaTiO ₃ *	-	0.419	Stable	-

** ref 55 * ref 20

Thermodynamic properties

The thermodynamic qualities of the materials' vibrational energies, vibrational free energies, entropies, and fixed volume heat capacities are computed within the temperature range of 0 to 800 K for MgHfS₃, MgZrS₃, and MgTiS₃, as illustrated in Figures 6 and 7 for MgHfS₃ and MgZrS₃, while MgTiS₃ exhibits a Debye temperature of zero. The variational trends between MgHfS₃ and MgZrS₃ are nearly identical. According to the pseudo-potential used, the specific heat capacities (Cv) for MgHfS₃ and MgZrS₃ are 115 and 112 JK⁻¹Nmol⁻¹, respectively. The similarity of these values at ambient temperature renders the compounds suitable for applications under such conditions. An inverse relationship between vibrational free energy and temperature is observed for both MgHfS₃ and MgZrS₃, as depicted in Figures 6 and 7, making them effective cooling devices, such as refrigerants in freezers and air conditioners, as well as coolants in automobiles. Additionally, these material-based devices may serve as ferromagnetic materials. The pressure supports the temperature, as shown in Figure 3 for the pressure-volume relationship, while Figures 6 and 7 illustrate the pressure effect on thermodynamic properties, correlating the proportional relationship between pressure and temperature. The entropy of the materials increases with rising temperature, as both figures demonstrate continuous increases in entropy with temperature, validating the second law of thermodynamics.



Fig. 6. Showing: a) heat capacity variation with temperature; b) Debye entropy-temperature variation; c) vibrational free energy variations with temperature for MgHfS₃; d) Debye heat capacity- temperature variation for MgHfS₃



Fig. 7. Showing: a) heat capacity variation with temperature; b) Debye Entropy-temperature variation; c) vibrational free energy variations with temperature for MgHfS₃; d) Debye heat capacity- temperature variation for MgZrS₃

Conclusions

The theoretical research on the structural, mechanical, and thermal properties of magnesium chalcogenide compounds, specifically MgBS₃ (where B = Hf, Zr, and Ti), has been systematically investigated using first principles methods within the Generalized Gradient Approximation (GGA). Our analysis of the elastic constants and mechanical properties reveals the significant stability—both mechanical and thermodynamic—and ductile characteristics of MgHfS₃ and MgZrS₃. In contrast, MgTiS₃ is identified as an unstable and brittle perovskite material. These findings suggest that our materials could serve as superior alternatives for those facing issues with stability and reliability, potentially enhancing their longevity. Furthermore, based on our results, particularly regarding mechanical and thermal properties, these chalcogenide perovskite materials are well-suited for various applications, including photovoltaics, coolants, refrigerants, ferromagnetic devices, and optoelectronic devices. Density Functional Theory (DFT) analysis indicates their highly favourable thermal stability and environmental sustainability for photovoltaic applications. Therefore, additional efforts are necessary to synthesize and explore these transition metal chalcogenide perovskite materials for practical applications and future advancements in solar cell fabrication within the relevant temperature range.

References

 Fatimah, G. Purwiandono, A. Hidayat, S. Sagadevan, A. Kamari, Mechanistic insight into the adsorption and photocatalytic activity of a magnetically separable γ-Fe2O3/montmorillonite nanocomposite for rhodamine B removal: Chemical Physics Letters, 792, 2022, p. 139-410.

- [2] Arora, C. Chawla, A. Chandra, S. Sagadevan, S. Garg, Advances in the strategies for enhancing the photocatalytic activity of TiO2:Conversion from UV-light active to visiblelight active photocatalyst: Inorganic Chemistry Communications, 143, 2022, p.109700.
- [3] S. Munusamy, RP. Sivasankaran, K. Sivaranjan, P. Sabhapathy, V. Narayanan, F. Mohammad, et al. Gallium nitride-polyaniline-polypyrrole hybrid nanocomposites as an efficient electrochemical sensor for mebendazole detection in drugs: Electrochimica Acta. 448, 2023, p. 142148.
- [4] R. Sivasamy, S. Amirthaganesan, R. Espinoza-González, F. Quero, KM. Batoo, *First-principles investigation of the electronic structure, optical and thermodynamic properties on monolayer Sn0.5Ge0.5Se nanosheet:* Physica E: Low-dimensional Systems and Nanostructures, 126, 2021, p. 114454.
- [5] R. Sekar, R. Sivasamy, B. Ricardo, P. Manidurai, Ultrasonically synthesized TiO2/ZnS nanocomposites to improve the efficiency of dye sensitized solar cells: Materials Science in Semiconductor Processing, 132, 2021, p.105917.
- [6] M.H. Miah, M.B. Rahman, M. Nur-E-Alam, N. Das, NB. Soin, SFWM. Hatta, et al. Understanding the degradation factors, mechanism and initiatives for highly efficient perovskite. Solar Cells, 9, 2023, p. 20220047125.
- [7] R. Brenes, D. Guo, A. Osherov, N. K. Noel, C. Eames, E. M. Hutter, S. K. Pathak, F. Niroui, R. H. Friend, M. S. Islam, H. J. Snaith, V. Bulović, T. J. Savenije, S. D. Stranks, Joule, 1, 2017,155.
- [8] J. J. Yoo, G. Seo, M. R. Chua, T. G. Park, Y. Lu, F. Rotermund, Y.-K. Kim, C. S. Moon, N. J. Jeon, J.-P. Correa-Baena, V. Bulović, S. S. Shin, M. G. Bawendi, J. Seo, Nature, 590, 2021, p.587.
- [9] E. H. Jung, N. J. Jeon, E. Y. Park, C. S. Moon, T. J. Shin, T.-Y. Yang, J. H. Noh, J. Seo, Nature, 567, 2019, 511.
- [10] M. A. Green, E. D. Dunlop, J. Hohl-Ebinger, M. Yoshita, N. Kopidakis, X. Hao, Prog. Photovoltaics, 28, 2020, 629.
- [11] L. A. Zafoschnig, S. Nold, J. C. Goldschmidt, IEEE : J. Photovoltaics, 10, 2020, 1632.
- [12] Oxford PV hopes to deliver perovskite-silicon tandem solar cells within a year | Perovskite-Info, <u>https://www.perovskite-info.com/oxford-pv-hopes-deliver-perovskite-silicon-tandem-</u> solar-cells within-year (accessed: November 2020).
- [13] Dubey, N. Adhikari, S. Mabrouk, F. Wu, K. Chen, S. Yang, Q. Qiao, J. Mater. Chem. A, 6, 2018, 2406.
- [14] H. Xie, M. Lira-Cantu, J. Phys. Energy, 2, 2020, 024008.
- [15] Q. Wang, N. Phung, D. D. Girolamo, P. Vivo, A. Abate, Energy Environ. Sci., 12, 2019, 865.
- [16] B. Chen, J. Song, X. Dai, Y. Liu, P. N. Rudd, X. Hong, J. Huang, Adv. Mater., 31, 2019, 1902413.
- [17] N. Phung, A. Abate, Small, 14, 2018, 1802573.
- [18] M. Fischer, M. Woodhouse, S. Herritsch, J. Trube, *International Technology Roadmap for Photovoltaic (ITRPV):* VDMA E. V. Photovoltaic Equipment, Frankfurt, Germany 2020.
- [19] R. Jeong, S. B. Choi, W. M. Kim, J.-K. Park, J. Choi, I. Kim, J. Jeong, Sci. Rep, 7, 2017, 15723.

- [20] Hajijafarassar, F. Martinho, F. Stulen, S. Grini, S. López-Mariño, M. Espíndola-Rodríguez, M. Döbeli, S. Canulescu, E. Stamate, M. Gansukh, S. Engberg, A. Crovetto, L. Vines, J. Schou, O. Hansen, Sol. Energy Mater. Sol. Cells, 207, 2020, 110334.
- [21]H.I. Eya, N.Y. Dzade, Density functional theory insights into the structural, electronic, optical, surface, and band alignment properties of BaZrS₃ chalcogenide perovskite for photovoltaics: ACS Appl. Energy Mater, 6 (11), 2023, 5729–5738.
- [22] H. Hiroi, Y. Iwata, S. Adachi, H. Sugimoto, A. Yamada, *IEEE*: J. Photovoltaics, 6, 2016, 760.
- [23] L. H. Wong, A. Zakutayev, J. D. Major, X. Hao, A. Walsh, T. K. Todorov, E. Saucedo, J. Phys. Energy, 1, 2019, 032001.
- [24] S. Gharibzadeh, B. A. Nejand, M. Jakoby, T. Abzieher, D. Hauschild, S. Moghadamzadeh, J. A. Schwenzer, P. Brenner, R. Schmager, A. A. Haghighirad, L. Weinhardt, U. Lemmer, B. S. Richards, I. A. Howard, U. W. Paetzold, Adv. Energy Mater., 9, 2019, 1803699.
- [25] J. Keller, K. V. Sopiha, O. Stolt, L. Stolt, C. Persson, J. J. S. Scragg, T. Törndahl, M. Edoff, Prog. Photovoltaics., 28, 2020, 237.
- [26] M. Stolterfoht, P. Caprioglio, C. M. Wolff, J. A. Márquez, J. Nordmann, S. Zhang, D. Rothhardt, U. Hörmann, Y. Amir, A. Redinger, L. Kegelmann, F. Zu, S. Albrecht, N. Koch, T. Kirchartz, M. Saliba, T. Unold, D. Neher, Energy Environ. Sci., 12, 2019, 2778.
- [27] Swarnkar, W. J. Mir, R. Chakraborty, M. Jagadeeswararao, T. Sheikh, A. Nag, Chem. Mater., 31, 2019, 565.
- [28] M. Khalid, T.K. Mallick, *Stability and performance enhancement of perovskite solar cells: a review*: **Energies**, **16** (10), 2023, 4031.
- [29] Y. Nishigaki, T. Nagai, M. Nishiwaki, T. Aizawa, M. Kozawa, K. Hanzawa, Y. Kato,
 H. Sai, H. Hiramatsu, H. Hosono, H. Fujiwara, Sol. RRL, 4, 2020, 1900555.
- [30] K. Hanzawa, S. Innura, H. Hiramatsu, H. Hosono, J. Am. Chem. Soc., 141, 2019, 5343.
- [31] Y. Gao, K. Huang, C. Long, Y. Ding, J. Chang, D. Zhang, L. Etgar, M. Liu, J. Zhang, J. Yang, Flexible perovskite solar cells: From materials and device architectures to applications: ACS Energy Lett.,7 (4), 2022, 1412–1445.
- [32] Crovetto, R. Nielsen, M. Pandey, L. Watts, J. G. Labram, M. Geisler, N. Stenger, K. W. Jacobsen, O. Hansen, B. Seger, I. Chorkendorff, P. C. K. Vesborg, Chem. Mater., 31, 2019, 3359.
- [33] M.Z. Rahman, S.S. Hasan, N. Absar, M.S. Akter, M.A. Hasan, M.Z. Hasan, M.A.K. Zilani, M.A. Islam, DFT based computational investigations of the physical properties of Chalcogenide Perovskites CsXS₃ (X=P, Ta) for Optoelectronic and Photovoltaic Applications: Computational Condensed Matter, 2024, https://doi.org/10.1016/j.cocom.2024.e00964.
- [34] S. Niu, G. Joe, H. Zhao, Y. Zhou, T. Orvis, H. Huyan, J. Salman, K. Mahalingam, B. Urwin, J. Wu, Y. Liu, T. E. Tiwald, S. B. Cronin, B. M. Howe, M. Mecklenburg, R. Haiges, D. J. Singh, H. Wang, M. A. Kats, J. Ravichandran, Nat. Photonics, 12, 2018, 392.
- [35] M.Z. Qamar, Z. Khalid, R. Shahid, W.C. Tsoi, Y.K. Mishra, A.K.K. Kyaw, M. A. Saeed, Advancement in indoor energy harvesting through flexible perovskite photovoltaics for selfpowered IoT applications: Nano Energy, 129, 2024, 109994.

- [36] Y. Wu, G. Xu, J. Xi, Y. Shen, X. Wu, X. Tang, J. Ding, H. Yang, Q. Cheng, Z. Chen, In situ crosslinking-assisted perovskite grain growth for mechanically robust flexible perovskite solar cells with 23.4% efficiency: Joule, 7 (2), 2023, 398–415.
- [37] K. Srivishnu, M.N. Rajesh, S. Prasanthkumar, L. Giribabu, *Photovoltaics for indoor applications: Progress, challenges and perspectives*: Sol. Energy 2023 264 112057.
- [38] Li, H. Sun, D. Dou, S. Gan, L. Li, Bipolar pseudohalide ammonium salts bridged perovskite buried interface toward efficient indoor photovoltaics: Adv. Energy Mater, 24, 2024 2401883.
- [39] G.G. Njema, J.K. Kibet, S.M. Ngari, A review of interface engineering characteristics for high performance perovskite solar cells: Meas. Energy, (100005), 2024.
- [40] S. Perera, H. Hui, C. Zhao, H. Xue, F. Sun, C. Deng, N. Gross, C. Milleville, X. Xu, D. F. Watson, B. Weinstein, Y.-Y. Sun, S. Zhang, H. Zeng, Nano Energy, 22, 2016, 129.
- [41] Comparotto, A. Davydova, T. Ericson, L. Riekehr, M. V. Moro, T. Kubart, J. Scragg, ACS Appl. Energy Mater., 3, 2020, 2762.
- [42] S. Niu, H. Huyan, Y. Liu, M. Yeung, K. Ye, L. Blankemeier, T. Orvis, D. Sarkar, D. J. Singh, R. Kapadia, J. Ravichandran, Adv. Mater., 29, 2017, 1604733.
- [43] X. Wei, H. Hui, C. Zhao, C. Deng, M. Han, Z. Yu, A. Sheng, P. Roy, A. Chen, J. Lin, D. F. Watson, Y.-Y. Sun, T. Thomay, S. Yang, Q. Jia, S. Zhang, H. Zeng, Nano Energy, 68, 2020, 104317.
- [44] X. Wei, H. Hui, S. Perera, A. Sheng, D. F. Watson, Y.-Y. Sun, Q. Jia, S. Zhang, H. Zeng, ACS Omega, 5, 2020, 19.
- [45] T. Gupta, D. Ghoshal, A. Yoshimura, S. Basu, P. K. Chow, A. S. Lakhnot, J. Pandey, J. M. Warrender, H. Efstathiadis, A. Soni, E. Osei-Agyemang, G. Balasubramanian, S. Zhang, S.-F. Shi, T.-M. Lu, V. Meunier, N. Koratkar, Adv. Funct. Mater., 0, 2020, 2001387.
- [46] G.G. Njema, J.K. Kibet, S.M. Ngari, A review of chalcogenide-based perovskites as the next novel materials: Solar cell and optoelectronic applications, catalysis and future perspectives: Next Nanotechnology, 7, 2025, 100102. https://doi.org/10.1016/j.nxnano.2024.100102.
- [47] H. Shaili, M. Beraich, A. El hat, M. Ouafi, E. mehdi Salmani, R. Essajai, W. Battal, M. Rouchdi, M. Taibi, N. Hassanain, A. Mzerd, J. Alloys Compd., 851, 2021, 156790.
- [48] N. A. Moroz, C. Bauer, L. Williams, A. Olvera, J. Casamento, A. A. Page, T. P. Bailey, A. Weiland, S. S. Stoyko, E. Kioupakis, C. Uher, J. A. Aitken, P. F. P. Poudeu, Inorg. Chem., 57, 2018, 7402.
- [49] P.Y.D. Maulida, S. Hartati, Y. Firdaus, A.T. Hidayat, L.J. Diguna, D. Kowal, A. Bruno, D. Cortecchia, A. Arramel, M.D. Birowosuto, *Recent developments in low-dimensional heterostructures of halide perovskites and metal chalcogenides as emergent materials: Fundamental, implementation, and outlook:* Chem. Phys. Rev. 5 (1), 2024.
- [50] Liu, T. Yang, W. Cai, Y. Wang, X. Chen, S. Wang, W. Huang, Y. Du, N. Wu, Z. Wang, Flexible indoor perovskite solar cells by in situ bottom-up crystallization modulation and interfacial passivation:Adv. Mater., 23, 2024, 2311562.
- [51]Z. Wang, Y. Han, P. Liu, Y. Li, S. Xu, J. Xiang, R. N. Ali, F. Su, H. Zeng, J. Jiang, B. Xiang, Appl. Surf. Sci., 499, 2020, 143932.

- [52] Perdew J P, Ruzsinszky A, Csonka G I, Vydrov O A, Scuseria G E, Constantin L A, Phys. Rev. Lett., 100, 2008, 136406.
- [53] Forge, PS library. <u>http://qe-forge.org/gf/project/pslibrary/</u>2013.
- [54] K. Kuhar, A. Crovetto, M. Pandey, K. S. Thygesen, B. Seger, P. C. K. Vesborg, O. Hansen, I. Chorkendorff, K. W. Jacobsen, Energy Environ. Sci., 10, 2017, 2579.
- [55] M. Sheng, S. Wang, H. Zhu, Z. Liu and G. Zhou, Computational applications for the discovery of novel antiperovskites andchalcogenide perovskites: a review. Front.Chem, 12, 2024, 1468434 doi: 10.3389/fchem.2024.1468434.
- [56] N. Priyadarshini, S. Mansingh, K.K. Das, R. Mohanty, K. Parida, G. Barik, K. Parida, Single crystal perovskite an emerging photocatalytic and storage material: synthesis to applications via theoretical insight: Phys. Rep. 2024 1061 1–53.
- [57] H. Xie, W. Que, Solvothermal synthesis of SnO2 nanoparticles for perovskite solar cells application, Front. Chem, 12, 2024, 1361275.
- [58] S. Ma, S. Sansoni, T. Gatti, P. Fino, G. Liu, F. Lamberti, *Research progress on homogeneous fabrication of large-area perovskite films by spray coating*: Crystals, 13 (2), 2023, 216.
- [59] Z. Wang, G. Liang, S. Jiang, F. Wang, H. Li, B. Li, H. Zhu, A. Lu, W. Gong, Understanding the environmental impact and risks of organic additives in plastics: a call for sustained research and sustainable solutions: Emerg. Contam. 2024 100388.
- [60] Kokalj, Comp. Mater. Sci., 28, 2003, 155-168.
- [61] G. B. Jin, E. S. Choi, T. E. Albrecht-Schmitt, J. Solid State Chem., 182, 2009, 1075.
- [62] X. Zhu, R. Zhang, M. Li, X. Gao, C. Zheng, R. Chen, et al. PEDOT:PSS/CuCl composite hole transporting layer for enhancing the performance of 2D Ruddlesden- popper perovskite solar cell:, The Journal of Physical Chemistry Letters., 13, 2022, p. 6101-6109.
- [63] J. Heo, L. Yu, E. Altschul, B. E. Waters, J. F. Wager, A. Zunger, D. A. Keszler, Chem. Mater., 29, 2017, 2594.
- [64] J.-Y. Tang, C.-C. Er, X.Y. Kong, B.-J. Ng, Y.-H. Chew, L.-L. Tan, A.R. Mohamed, S.- P. Chai, Two-dimensional interface engineering of g-C3N4/g-C3N4 nanohybrid: synergy between isotype and pn heterojunctions for highly efficient photocatalytic CO₂ reduction, Chem. Eng. J. 2023 466 143287.
- [65] M.F.M. Noh, N.A. Arzaee, C.C. Fat, S.K. Tiong, M.A.M. Teridi, A.W.M. Zuhdi, Perovskite/CIGS Tandem solar cells: progressive advances from technical perspectives: Mat. Today Eergy, 2023, (101473).
- [66] Srivastava, R.K. Shukla, P. Srivastava, P. Chandra, N. Kumar, *Chalcogenides: bulk and thin films, Mater. Sci. A Field Divers:* Ind. Appl., 1 (25), 2023, 1–25.
- [67] Xu Y-F, Wu W-Q, Rao H-S, Chen H-Y, Kuang D-B, Su C-Y, CdS/CdSe co-sensitized TiO2 nanowire-coated hollow spheres exceeding 6% photovoltaic performance: Nano Energy, 11, 2015, p. 621-630.
- [68] M. Saiduzzaman, T. Ahmed, K.M. Hossain, A. Biswas, S. Mitro, A. Sultana, M. S. Alam, S. Ahmad, Band gap tuning of non-toxic Sr-based perovskites CsSrX₃ (X= Cl, Br) under pressure for improved optoelectronic applications: Mat. Today Commun., 34, 2023, 105188.
- [69] M.Z. Abbasi, A.U. Rehman, Z. Khan, O.U. Rehman, M.A. Saeed, *Analyzing the compatibility and optimization of organic and Al2CdX4 chalcogenides materials as charge*

transport layers for planar and inverted MASnI₃ perovskites: **Opt. Mater., 154,** 2024, 115789.

- [70] Tundwal, H. Kumar, B.J. Binoj, R. Sharma, G. Kumar, R. Kumari, A. Dhayal, A. Yadav, D. Singh, P. Kumar, *Developments in conducting polymer-, metal oxide and carbon nanotube-based composite electrode materials for supercapacitors: a review:* RSC Adv., 14 (14), 2024, 9406–9439.
- [71] G-X. Wang, X-X. Ren, J-J. Wei, A-J. Wang, T. Zhao, J-J. Feng, et al. Ultrasensitive PEC cytosensor for breast cancer cells detection and inhibitor screening based on plum-branched CdS/Bi2S3 heterostructures: Bioelectrochemistry, 152, 2023, p. 108442.
- [72]G.G. Njema, J.K. Kibet. A review of the technological advances in the design of highly efficient perovskite solar cells: International Journal of Photoenergy, 2023, 2023, p. 3801813.
- [73] LMM. Livingston, AGS. Raj, RT. Prabu, A. Kumar, Computational analysis of FeS2 material for solar cell application: Optical and Quantum Electronics, 55, 2023, p. 244.
- [74] NAY. Razamin, HJ. Woo, T. Winie, Comparative study of nickel selenide, iron selenide and platinum on triiodide reduction for dye-sensitized solar cells: Optical Materials: X, 13, 2022, p. 100119.
- [75] W. Genshun, Y. Shi, P. Fuguo, H. Chengjian, Q. Minghao, L. Junxiong, et al. Silicon heterojunction solar cells with up to 26.81% efficiency achieved by electrically optimized nanocrystalline-silicon hole contact layers: Nature Energy, 13, 2023, p. 789-799.
- [76] Machín, F. Marquez, Advancements in photovoltaic cell materials: silicon, organic, and perovskite solar cells: Materials, 17 (5), 2024, 1165.
- [77] Xu, M. Zhang, Z. Li, X. Yang, R. Zhu, Challenges and perspectives toward future widebandgap mixed-halide perovskite photovoltaics: Adv. Energy Mater, 13 (13), 2023, 2203911.
- [78] M. Verma, GP. Mishra, Analytical model of InP QWs for efficiency improvement in GaInP/Si dual junction solar cell: Physica Status Solidi A, 220, 2023, p. 2200500.
- [79] L. Zhu, Y. Wang, X. Pan, H. Akiyama, Theoretical modeling and ultra-thin design for multijunction solar cells with a light-trapping front surface and its application to InGaP/GaAs/InGaAs 3-junction: Optics Express, 30, 2022, p. 35202-35218.
- [80] B. Fadila, M. Ameri, D. Bensaid, M. Noureddine, I. Ameri, S. Mesbah, & Y. Al-Douri, Journal of Magnetism and Magnetic Materials, 448, 2018, 208–220. doi:10.1016/j.jmmm.2017.06.0.
- [81] Xue, J. Wang, Q. Wu, L. Zhang, R. Dai, B. Tian et al, Results in Physics, 19, 2020, 103596
- [82] M. Palumbo and A. Dal Corso, Physica Status Solidi B 254, 2017, 1700101.
- [83] Z. Ye, H. Sun, H. Gao, L. Sun, J. Guo, Y. Jiang, C. Wu, S. Zheng, *Intrinsic activity regulation of metal chalcogenide electrocatalysts for lithium–sulfur batteries:* Energy Storage Mater., 60, 2023, 102855.
- [84] S. Khatoon, S.K. Yadav, V. Chakravorty, J. Singh, R.B. Singh, M.S. Hasnain, S. M. Hasnain, Perovskite solar cell's efficiency, stability and scalability: a review: Mater. Sci. Energy Technol., 6, 2023, 437–459.

- [85] N. Priyadarshini, S. Mansingh, K.K. Das, R. Mohanty, K. Parida, G. Barik, K. Parida, Single crystal perovskite an emerging photocatalytic and storage material: synthesis to applications via theoretical insight: Phys. Rep., 1061, 2024, 1–53.
- [86] R.O Balogun, M.A Olopade, O.O Oyebola, & A. D Adewoyin, Materials Science and Engineering B: Solid-State Materials for Advanced Technology, 273, 2021, 115405. <u>https://doi.org/10.1016/j.mseb.2021.115405.</u>
- [87] Rahul Yadav, Anshuman Srivastava, Jisha Annie Abraham, Ramesh Sharma, Sajad Ahmad Dar, Materials Science and Engineering: B Volume, 283, 2022, 0921-5107, https://doi.org/10.1016/j.mseb.2022.115781.

Received: October 07, 2024 Accepted: March 12, 2025