

Article

First-Principles Study of Two-Dimensional A_2SnI_4 ($A = MA$, DMA , GUA) Ruddlesden–Popper Perovskites

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Abstract

Two-dimensional (2D) Ruddlesden–Popper (RP) tin halide perovskites have attracted considerable attention as lead-free photovoltaic absorbers; however, the impact of organic A-site cations on their structure and pressure-dependent optoelectronic behavior remains underexplored. In this study, density functional theory (DFT) is used to investigate the structural, electronic, and optical properties of A_2SnI_4 ($A = GUA^+$, DMA^+ , MA^+) under ambient conditions and under hydrostatic pressure. All three compounds adopt layered frameworks in which the organic cations occupy the interlayer region, while SnI_6 octahedra form the inorganic slabs. Band-gap calculations are performed using HSE06 for ambient pressure, known for its accuracy in electronic structure predictions, and PBE for pressure simulations, due to its computational efficiency in large-scale systems. At ambient pressure, Hybrid-functional (HSE06) calculations indicate that all three materials are direct-gap semiconductors, with band gaps of 2.25 eV for MA_2SnI_4 , 2.98 eV for DMA_2SnI_4 , and 2.85 eV for GUA_2SnI_4 . Under hydrostatic compression, DMA_2SnI_4 shows comparatively modest band-gap variation and saturates near 1.7 eV. In contrast, GUA_2SnI_4 and MA_2SnI_4 exhibit pronounced band-gap narrowing, including a pressure-induced direct-to-indirect transition near 2 GPa, with band gaps decreasing to 0.59 eV (GUA_2SnI_4) and 0.34 eV (MA_2SnI_4) at elevated pressures. Overall, these findings highlight that A-site chemistry, combined with hydrostatic pressure, enables tuning the electronic and optical responses in tin-based 2D RP perovskites, demonstrating their promise as tunable, lead-free photovoltaic absorbers.

Keywords: two-dimensional perovskites; pressure-induced effects; 2D Ruddlesden–Popper perovskites; density functional theory



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1. Introduction

Halide perovskites have emerged as highly promising materials for photovoltaic and optoelectronic applications due to their strong light absorption, tunable band gaps, and excellent charge-transport properties [1–3]. Lead-based perovskite solar cells (PSCs) have achieved power conversion efficiencies (PCEs) exceeding 26% [4,5], with benchmark materials like $MAPbBr_3$ and $MAPbI_3$ [6–8]. However, concerns over Pb toxicity have intensified

efforts to develop lead-free or low-lead alternatives [9,10]. A prominent strategy involves B-site (Pb^{2+}) substitution with less toxic divalent cations such as Sn^{2+} or Ge^{2+} , which preserve favorable valence-band features and visible-light absorption. A-site substitution with alkali metal cations (e.g., Cs^+ , Rb^+ , K^+) plays a pivotal role in these lead-free systems, effectively modulating structural distortions and electronic properties [11–14]. Investigations of alternative halide perovskites, including those with Ca-, Sr-, Ba-, RbSnX_3 or CsGeX_3 ($\text{X} = \text{Cl}$, Br , I), have further demonstrated the strong light absorption, high optical conductivity, and substantial band-gap tunability in lead-free perovskite [15–19].

Within this broad landscape of A-site engineering for lead-free halide perovskites, guanidinium (GUA^+) has emerged as a highly promising organic spacer due to its planar, highly symmetric structure and multiple NH_2 groups, which facilitate strong hydrogen bonding and exert significant geometric influences on the inorganic layers [20]. Mixed-cation perovskites compositions incorporating GUA^+ with MA^+ , FA^+ , or inorganic cations have demonstrated enhanced optical absorption, extended carrier lifetimes, and optimized band-edge alignments [21,22]. GUA -based perovskites have also achieved competitive PCEs above 19%, with pronounced excitonic characteristics and reduced nonradiative recombination [23]. Furthermore, experimental studies further reveal that GUA -containing precursors preferentially form layered 2D perovskite phases of GUA_2BX_4 , underscoring its role in engineering Sn–I frameworks, particularly through strong interactions with under-coordinated anions and interfaces [24]. 2D metal halide perovskites provide a rich compositional and structural phase space owing to their alternate organic–inorganic layering, allowing precise control over their optical and electronic properties. Among these, the [100]-oriented RP family, $\text{A}'_2\text{A}_{n-1}\text{B}_n\text{X}_{3n+1}$, features inorganic perovskite slabs separated by organic spacer cations (A'), offering a versatile platform where the selection of A' and A cations profoundly influence band-gap behavior, lattice geometry, and interlayer coupling [25,26]. These materials are particularly attractive for lead-free optoelectronic applications, benefiting from extensive chemical flexibility and low-temperature processability [27].

First-principles investigations on related oxide Ruddlesden–Popper (RP) compounds, such as monolayer Sr_2TiO_4 and Ba_2TiO_4 , have demonstrated that dimensional reduction enhances quantum confinement and enables highly tunable structural, electronic, and optical properties, highlighting the broader potential of layered perovskite architectures [28]. Recent research on halide RP perovskites such as $(\text{DMA})_2\text{PbBr}_4$, $(\text{MHy})_2\text{PbBr}_4$, and $(\text{EA})_2\text{PbBr}_4$ has revealed that lower dimensionality relaxes traditional Goldschmidt tolerance-factor constraints, accommodating larger organic A-site cations and yielding distinct structural and electronic behavior compared to their three-dimensional counterparts [29]. Complementary first-principles studies on $\text{BA}_2\text{MA}_{n-1}\text{B}_n\text{X}_{3n+1}$ ($\text{B} = \text{Ge}$ or Sn ; $\text{X} = \text{Br}$ or I ; $n = 1$ –5) RP perovskites and their 3D $(\text{MA})\text{BX}_3$ analogs have revealed that smaller B-site cations cause anisotropic distortions and systematic band-gap variations across the series, and have identified the $n = 1$ iodide BA_2SnI_4 as a particularly favorable lead-free RP compound with promising electronic characteristics [30]. Despite these advances, a systematic first-principles comparison of different organic A-site cations in Sn-based 2D RP perovskites of the form A_2SnI_4 remains absent. GUA^+ , DMA^+ , and MA^+ represent three chemically distinct organic cations capable of generating markedly different inorganic environments around the SnI_6 octahedra, and their relative influence on lattice structure, band-edge alignment, dielectric screening, and optical response has not yet been elucidated.

In addition to compositional and structural tuning via A-site engineering, hydrostatic pressure offers a complementary, reversible strategy for modulating halide perovskite properties. Compression reduces lattice parameters and crystal volume displacing cations

and anions while inducing tilts and rotations in the BX_6 octahedra [31–33]. Previous high-pressure studies on inorganic halide perovskites, such as $CsGeCl_3$, $CsGeI_3$, $KCaCl_3$, and $RbYbF_3$, have shown that such distortions drive significant band-gap narrowing and improved conductivity, establishing pressure as a powerful tool for optoelectronic optimization [34–37]. This pressure-dependent tunability further enhances the potential of lead-free perovskites as versatile absorber materials for high-performance, environmentally sustainable solar cells.

In this study, a comprehensive first-principles investigation is carried out on layered, tin-based RP perovskites: A_2SnI_4 , in which $A = GUA^+$, DMA^+ , and MA^+ , with a primary focus on the critical role of organic A-site cation engineering in dictating lattice geometry, electronic structure, and optical properties within these two-dimensional Sn–I frameworks. By systematically comparing these chemically distinct A-site cations, we elucidate their influence on the structural stability, band-edge characteristics, and dielectric response of these lead-free materials, evaluating their potential as tunable light absorbers for photovoltaic applications. Furthermore, we explore the effects of hydrostatic pressure on these systems, examining pressure-induced structural distortions, octahedral tilting, and band-edge evolution. Through detailed analysis of structural, electronic, and optical properties under ambient and high-pressure conditions, this work uncovers how A-site chemistry interacts with external compression to enable precise, reversible tuning of optoelectronic performance. These findings establish key design guidelines for lead-free 2D RP perovskites (A_2SnI_4) and provide deeper insights into their promise as environmentally sustainable, high-performance absorbers for next-generation solar cells.

2. Results and Discussion

2.1. Structure Properties of 2D Perovskites

Figure 1A–C illustrates the optimized crystal structures of three layered tin-based Ruddlesden–Popper perovskites. Despite sharing the same inorganic Sn–I backbone, the three systems exhibit noticeable differences in the orientation, size, and packing of the organic A-site cations. In GUA_2SnI_4 , the larger guanidinium cations induce a more expanded interlayer spacing and stronger hydrogen-bonding interactions with the surrounding iodide ions. In contrast, DMA_2SnI_4 and MA_2SnI_4 feature progressively smaller organic cations, leading to a more compact lattice and reduced organic–inorganic separation. These variations in A-site chemistry are expected to influence lattice distortions, octahedral tilting, and interlayer coupling.

2.2. Electronic Band Structure

The electronic behavior of a material can be understood effectively through its band structure and density of states (DOS). The total and partial DOS (TDOS and PDOS) enable the identification of contributions from different atomic orbitals and provide insight into the nature of the electronic states near the Fermi level. Optical absorption was evaluated using Fermi's Golden Rule, which determines the probability of electronic transitions from occupied to unoccupied states. Electrical conductivity, on the other hand, is governed by the concentration and mobility of charge carriers, primarily electrons and holes. These properties depend on the carrier density and their effective masses, where a lower effective mass typically enhances carrier mobility and thus conductivity.

Figure 2 displays the HSE06 band structures of the DMA_2SnI_4 , GUA_2SnI_4 , and MA_2SnI_4 monolayers, respectively, illustrating the dominant orbital contributions to the valence and conduction bands. The band structures further clarify the distribution of occupied and unoccupied electronic states and enable classification of the band gap. A direct band gap occurs when the valence-band maximum (VBM) and conduction band

minimum (CBM) lie at the same k-point in the Brillouin zone; otherwise, the band gap is indirect. The HSE06 calculations reveal that all three materials exhibit direct band gaps, with values of 2.85 eV for GUA_2SnI_4 , 2.98 eV for DMA_2SnI_4 , and 2.25 eV for MA_2SnI_4 , highlighting their potential for optoelectronic applications.

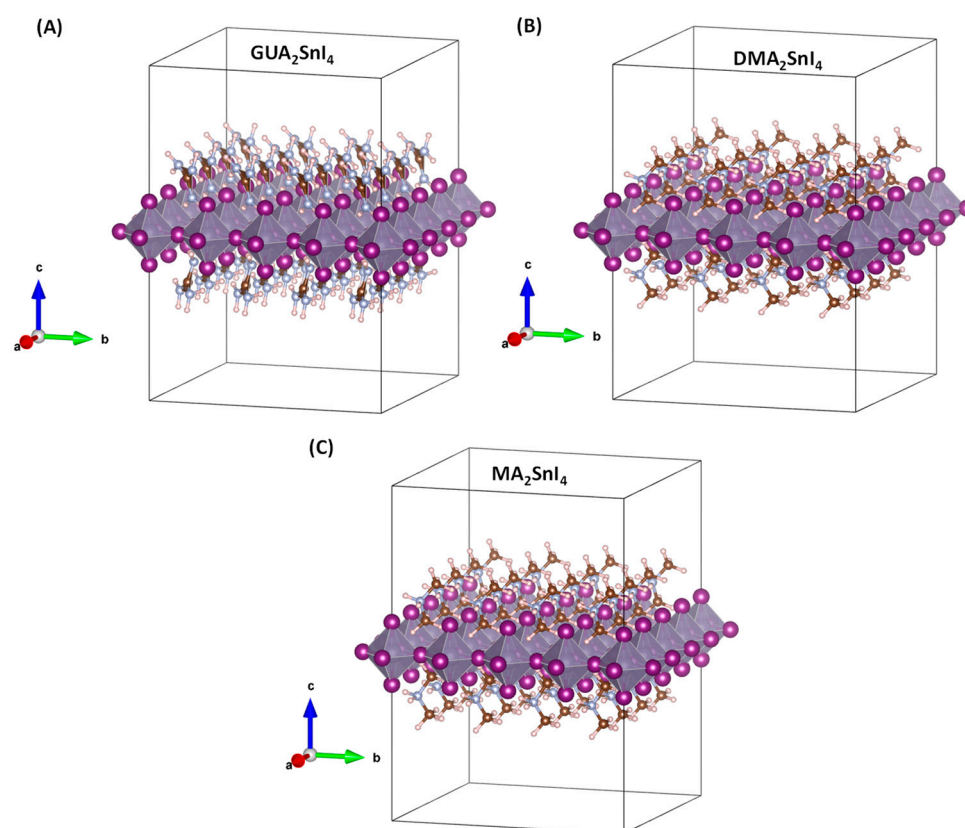


Figure 1. Crystal structures of the X_2SnI_4 materials: (A) GUA_2SnI_4 , (B) DMA_2SnI_4 , and (C) MA_2SnI_4 .

Figures 3, S1 and S2 display the HSE06 projected density of states (PDOS) of the DMA_2SnI_4 , GUA_2SnI_4 , and MA_2SnI_4 monolayers. The PDOS of the 2D DMA_2SnI_4 monolayer reveals that the VBM is predominantly composed of I-5p states with a minor contribution from Sn-5s orbitals, indicating strong Sn–I hybridization. In contrast, the CBM is mainly derived from Sn-5p states, with negligible contributions from the organic DMA cation. This confirms that the electronic states near the band edges are governed primarily by the inorganic Sn–I framework, while the organic cation plays a structural and electrostatic role rather than directly participating in charge transport. Such orbital characteristics are favorable for efficient carrier transport and optoelectronic performance.

The band gaps were further evaluated using the PBE-GGA functional under varying hydrostatic pressures. The results show that the fundamental features of the electronic structure in X_2SnI_4 ($\text{X} = \text{GUA}, \text{DMA}, \text{MA}$) remain largely preserved for DMA_2SnI_4 and MA_2SnI_4 at 4 and 6 GPa. In general, the band gap decreases as pressure increases, driven by the downward shift in the CBM toward the Fermi level. Table 1 and Figures 4, S3 and S4 show the effect of hydrostatic pressure on the GGA-PBE band gaps of MA_2SnI_4 , GUA_2SnI_4 , and DMA_2SnI_4 perovskite materials, respectively. At ambient pressure (0 GPa), the materials exhibit direct band gaps of 2.31 eV (GUA_2SnI_4), 2.38 eV (DMA_2SnI_4), and 1.88 eV (MA_2SnI_4). With increasing pressure, all compounds show a continuous band-gap reduction, with GUA_2SnI_4 experiencing a more pronounced decrease, reaching 1.70 eV.

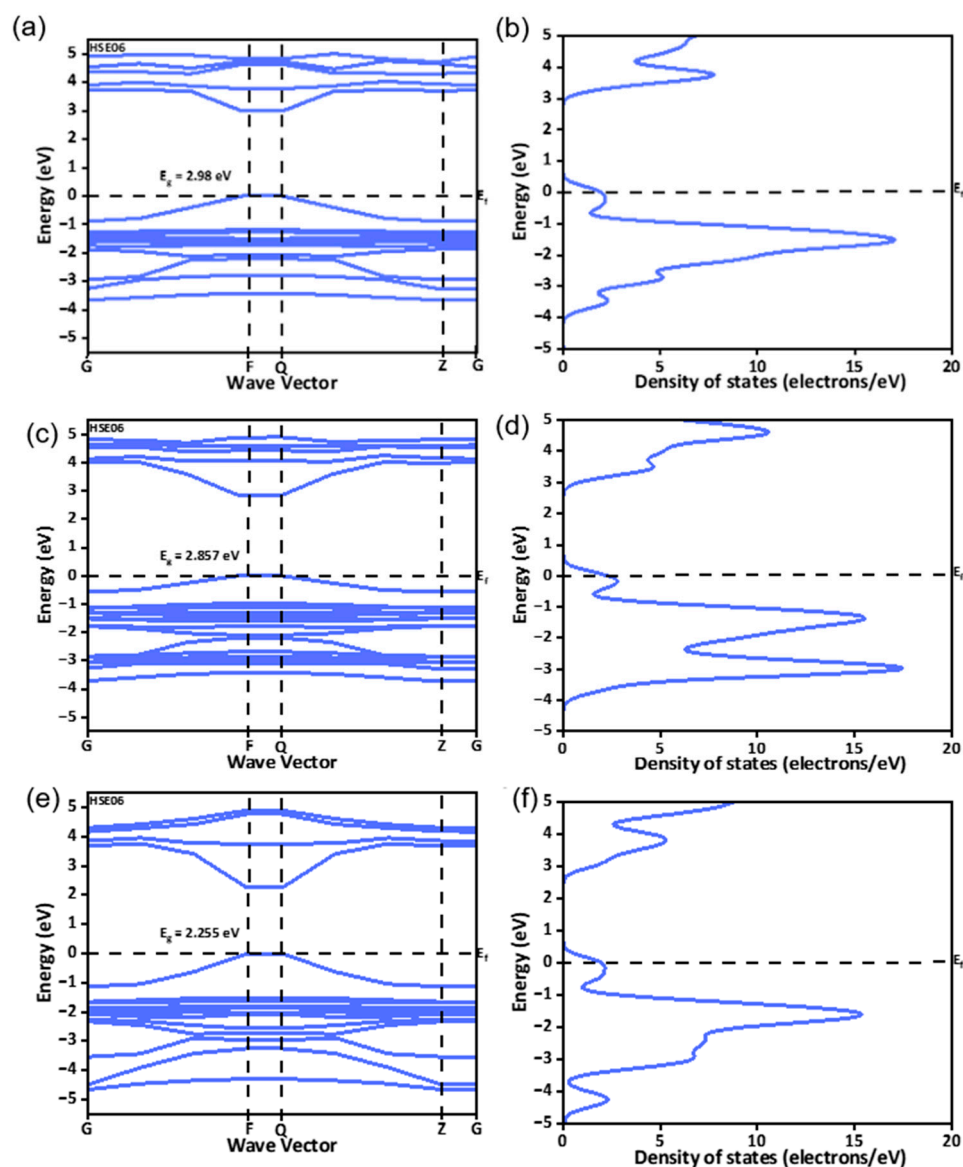


Figure 2. HSE06 band structures and DOS of (a,b) DMA₂SnI₄; (c,d) GUA₂SnI₄; and (e,f) MA₂SnI₄.

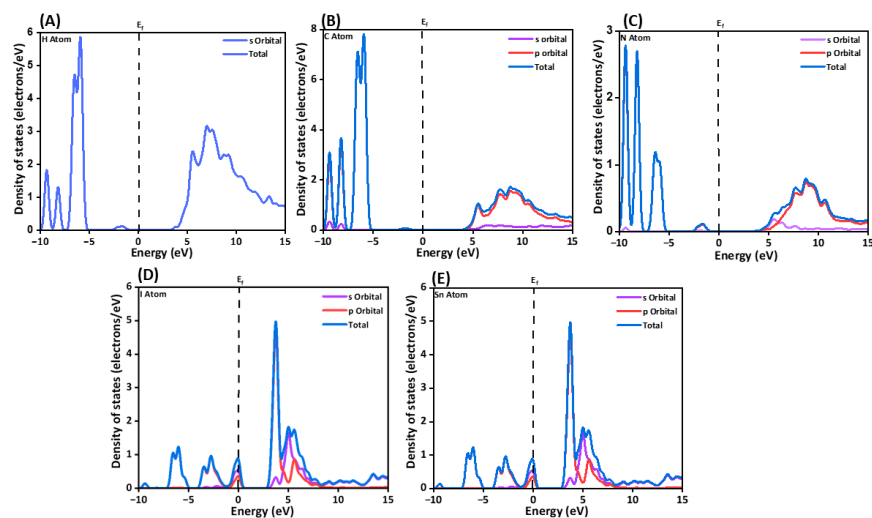
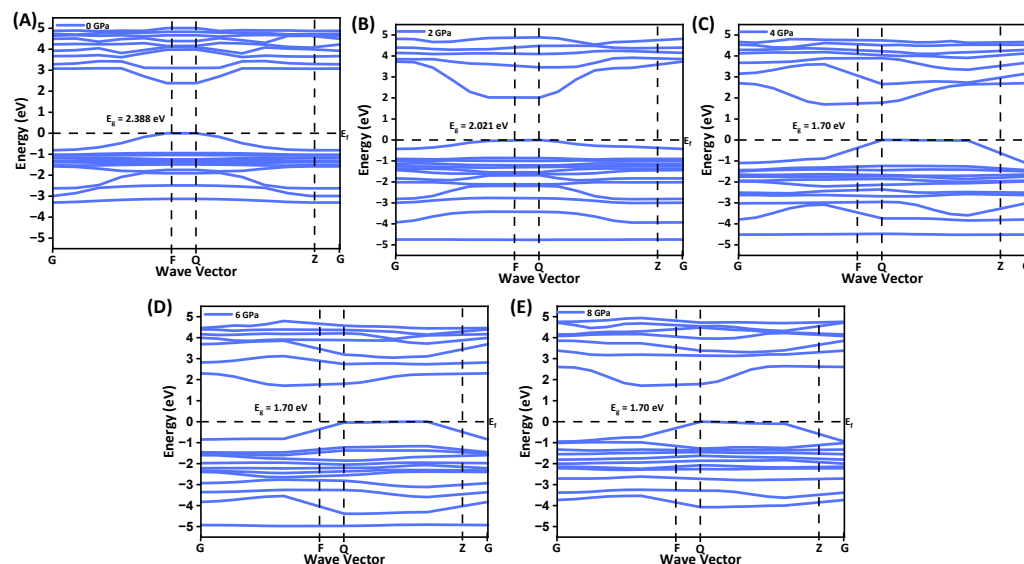


Figure 3. HSE06-calculated projected density of states (PDOS) of the 2D DMA₂SnI₄ monolayer with the Fermi level set at 0 eV: (A) H atom, (B) C atom, (C) N atom, (D) I atom, and (E) Sn atom.

Table 1. The effect of pressure on the band gaps of MA₂SnI₄, DMA₂SnI₄, and GUA₂SnI₄ perovskites.

Pressure (GPa)	MA ₂ SnI ₄	DMA ₂ SnI ₄	GUA ₂ SnI ₄
0 GPa	1.886	2.388	2.314
2 GPa	0.679	2.021	1.814
4 GPa	0.55	1.70	1.028
6 GPa	0.55	1.70	1.015
8 GPa	0.34	1.70	0.59

**Figure 4.** GGA-PBE band gap of DMA₂SnI₄ under hydrostatic pressure: (A) 0 GPa, (B) 2 GPa, (C) 4 GPa, (D) 6 GPa, and (E) 8 GPa.

For DMA₂SnI₄, the gap remains unchanged at 1.70 eV at 4–8 GPa, while MA₂SnI₄ shows a similar stability at 4 and 6 GPa below 8 GPa. For DMA₂SnI₄ and MA₂SnI₄, the band-gap evolution in the 4–6 GPa range is primarily controlled by lattice compression, beyond which further pressure induces only minor modifications in the electronic structure, reflecting a saturation of pressure-driven electronic adjustments [38]. At 8 GPa, however, the structural effects become more pronounced. GUA₂SnI₄ and MA₂SnI₄ undergo more significant lattice compression, leading to stronger orbital overlap between the Sn and I atoms. This increased overlap leads to a substantial narrowing of the band gap and results in a transition from direct to indirect band gap for both materials. On the other hand, DMA₂SnI₄ exhibits less lattice compression at 8 GPa due to its longer Sn–I bond length and more flexible organic cation structure, maintaining a stable electronic structure and no significant reduction in the band gap. At high pressure, the calculated stabilized gaps are 0.59/1.70/0.34 eV for GUA₂SnI₄, DMA₂SnI₄, and MA₂SnI₄, respectively. Notably, at 2 GPa, the band-gap character transitions from direct to indirect. Between 4 and 8 GPa, the gap further decreases from 1.02 to 0.59 eV for GUA₂SnI₄ and from 0.55 to 0.34 eV for MA₂SnI₄. This trend reflects the lattice compression induced by hydrostatic pressure, which enhances orbital overlap and consequently narrows the band gap.

The lattice's structural characteristics primarily determine the pressure-induced changes in electronic properties. Table 2 represents bond distance (Å) for Sn–I, C–N, and H–N bonds in GUA₂SnI₄, DMA₂SnI₄, and MA₂SnI₄. At 0 GPa, the Sn–I bond lengths in GUA₂SnI₄ and MA₂SnI₄ shorten significantly to 2.91 Å and 2.90 Å, respectively, enhancing orbital overlap and contributing to band-gap reduction and reduced pressure sensitivity. However, DMA₂SnI₄ shows a less pronounced compression, with a Sn–I bond length of 3.01 Å, resulting in a more stable band gap under high pressure. Differences

in C–N and H–N bond lengths indicate variations in organic cation rigidity, influencing interlayer packing and pressure-induced lattice compressibility.

Table 2. Calculated bond lengths (Å) for GUA₂SnI₄, DMA₂SnI₄, and MA₂SnI₄.

Structure	I–Sn (Å)	C–N (Å)	H–N (Å)
GUA ₂ SnI ₄	2.91	1.33	1.01
DMA ₂ SnI ₄	2.90	1.49	1.09
MA ₂ SnI ₄	3.01	1.52	1.09

2.3. Optical Properties

It is important to note that the CBM and VBM occur at the same k-point in the Brillouin zone, confirming the direct band-gap nature of these materials. This direct gap, combined with their favorable electronic characteristics, supports their suitability for optoelectronic device applications. The optical and dielectric responses of the X₂SnI₄ (X = GUA, DMA, MA) monolayers were examined to assess their performance under photon excitation, focusing on their absorption characteristics across various photon energies and pressures. The interaction between electrons and incident photons plays a central role in determining the optical response of the synthesized materials [39]. From these components, the absorption coefficient and refractive index can be extracted, providing insight into light–matter interactions. Materials that interact strongly with electromagnetic radiation often exhibit non-linearities or variations in energy exchange [40].

2.3.1. Absorption Spectrum

The lead-free perovskites X₂SnI₄ (X = GUA, DMA, MA) exhibit favorable optical absorption and moderate optical conductivity [41], making them promising candidates for photovoltaic applications. Analysis of Figures 5A, S5a and S6a indicates that absorption in X₂SnI₄ (X = GUA, DMA, MA) begins at energies above 0 eV, reflecting the intrinsic band gap of each compound. At ambient pressure, absorption in GUA₂SnI₄ initiates in the visible region (~2–3 eV) and progressively increases with applied hydrostatic pressure. Notably, significant absorption peaks are observed between 8 and 15 eV, with initial peaks occurring in the visible range and the most prominent peaks in the ultraviolet region (7–18 eV). These features suggest that the materials can efficiently absorb both visible and UV photons, which is critical for photovoltaic applications, as UV absorption enhances the utilization of high-energy photons and contributes to improved energy conversion efficiency.

In X₂SnI₄ (X = DMA, MA), the optical absorption steadily increases, with prominent peaks observed between 8 and 20 eV. Two major peaks appear in the high ultraviolet region, approximately at 8–10 eV and 12–20 eV. Notably, pressure induces a shift in the onset of absorption, with more intense peaks occurring at higher energies (7–18 eV for DMA₂SnI₄ and 7–16 eV for MA₂SnI₄). This behavior highlights their capability to absorb a broad spectrum of photon energies relevant for photovoltaic and optoelectronic applications.

2.3.2. Loss Function

Figures 5B, S5b and S6b present the energy loss spectra (L) of X₂SnI₄ (X = GUA, DMA, MA), which represent the energy dissipated by electrons during collisions while traversing the material. The plasma frequency (ω_p) corresponds to the peak of the loss function and is indicative of plasma resonance [42]. At ambient pressure (0 GPa), the first prominent peak in the loss spectrum appears at 9.9 eV, 9.82 eV, and 9.77 eV for X = GUA, DMA, and MA, respectively. Upon increasing pressure to 8 GPa, these peaks shift to higher energies, reflecting an increase in the plasma frequency. This trend suggests that the largest energy loss occurs in the ultraviolet region, where photon energy exceeds the band gap.

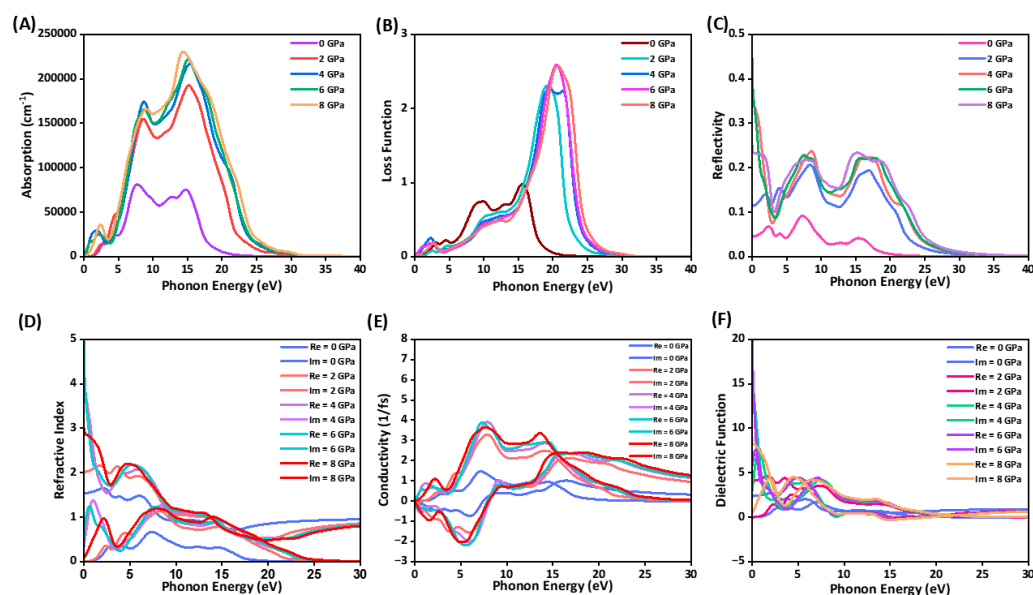


Figure 5. The calculated (A) absorption; (B) loss function; (C) reflectivity; (D) refractive index; (E) conductivity; and (F) dielectric function for 2D DMA₂SnI₄ under hydrostatic pressure.

2.3.3. Reflectivity

The surface optical properties of X₂SnI₄ (X = GUA, DMA, MA) were evaluated through their reflectivity spectra, which characterize the interaction of incident light with the material [43]. At ambient pressure (0 GPa), GAU₂SnI₄ exhibits a static reflectance peak R(0) of 0.048 at 0 eV, corresponding to 4.8% of reflected light, indicating minimal reflectivity. Similarly, DMA₂SnI₄ and MA₂SnI₄ show peak reflectance values of 0.049 and 0.051 at 0 eV, reflecting 4.9% and 5.2% of the incident light, respectively. These results indicate that GAU₂SnI₄ has slightly lower reflectivity compared to the other compounds under identical pressure conditions. Upon increasing hydrostatic pressure to 8 GPa, notable shifts in peak reflectance are observed. GAU₂SnI₄ shows a maximum reflectance of 0.291 at 9.87 eV, while DMA₂SnI₄ and MA₂SnI₄ exhibit peak values of 0.22 at 7.25 eV, as shown in Figures 5C, S5c and S6c. These changes indicate that pressure modifies the optical response of X₂SnI₄, enhancing reflectivity at higher photon energies and altering the material's interaction with light across different energies and angles.

2.3.4. Refractive Index

The refractive index spectra of DMA₂SnI₄, GUA₂SnI₄, and MA₂SnI₄ exhibit similar dispersion behavior while showing clear material- and pressure-dependent differences. According to Figures 5D, S5d and S6d, the real part of the refractive index is relatively high in the low-energy region, where pronounced peaks and shoulders appear due to strong optical transitions, and then gradually decreases with increasing photon energy, approaching nearly constant values at higher energies. External pressure from 0 to 8 GPa systematically enhances the refractive index in the low-energy region and modifies the intensity and position of the main spectral features, indicating increased electronic polarizability under compression. Among the materials, MA₂SnI₄ displays the strongest pressure-induced enhancement and the most prominent low-energy dispersion, while GUA₂SnI₄ shows intermediate behavior with closely spaced features in the low-energy range. In contrast, DMA₂SnI₄ presents comparatively weaker dispersion and a more gradual response to pressure. These results highlight the significant role of both pressure and organic cation choice in tuning the refractive index and optical properties of layered tin iodide perovskites.

2.3.5. Conductivity

The optical conductivity spectra of DMA_2SnI_4 , GUA_2SnI_4 , and MA_2SnI_4 exhibit comparable overall behavior, with clear differences in magnitude and pressure response. According to Figures 5E, S5e and S6e, the real part of the optical conductivity remains low at low photon energies, increases with pronounced peaks in the low-to-mid-energy region arising from allowed optical transitions, and then gradually decreases at higher energies. With increasing pressure from 0 to 8 GPa, the intensity of the main conductivity peaks is systematically enhanced, and their positions are slightly shifted, indicating an increase in charge carrier response and stronger optical transitions under compression. Among the compounds, MA_2SnI_4 shows the highest conductivity values and the most pronounced pressure-induced enhancement, reflecting its stronger sensitivity to structural compression. GUA_2SnI_4 displays intermediate conductivity with multiple overlapping features in the low-energy region, whereas DMA_2SnI_4 exhibits comparatively lower conductivity and a more gradual evolution with pressure. These results demonstrate that external pressure effectively tunes the optical conductivity of these layered tin iodide perovskites, with the extent of enhancement strongly dependent on the nature of the organic cation.

2.3.6. Dielectric Function

The dielectric function, $\varepsilon(\omega)$, is expressed as a combination of its real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ components [44], as defined in Equation (1).

$$\varepsilon(\omega) = \varepsilon_1(\omega) + \varepsilon_2(\omega) \quad (1)$$

The imaginary component of the dielectric function, $\varepsilon_2(\omega)$, is directly related to inter-band electronic transitions and therefore reflects the underlying band structure and density of states of the material. In contrast, the real component, $\varepsilon_1(\omega)$, describes the material's polarizability and its response to an external electromagnetic field. The Kramers–Kronig relations [45], formulated as quantum integrals, are commonly employed to obtain the real part of the dielectric function from its imaginary counterpart [46,47], as presented in Equations (2) and (3).

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

$$\varepsilon_2(\omega) = \frac{4}{\pi \omega^2} \sum_{nn'} \int |p_{nn'}(k)|^2 \frac{dS_k}{\nabla_{nn'}(ks)} \quad (3)$$

Figure 5F displays the real component $\varepsilon_1(\omega)$ of the dielectric function, showing that the static dielectric values at 8 GPa remain high for all studied materials. The maximum peak appears at zero photon energy, with $\varepsilon_1(0)$ reaching 8.110 eV for GUA_2SnI_4 and 2.924 eV for DMA_2SnI_4 and MA_2SnI_4 . A noticeable decrease in $\varepsilon_1(\omega)$ is observed between 8 and 10 eV across pressures from 0 to 8 GPa. The elevated $\varepsilon_1(\omega)$ values suggest strong polarization capability, indicating the suitability of these perovskites for optoelectronic and photovoltaic applications. The combined behavior of large $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ at lower photon energies, followed by reduced values at higher energies, further highlights their potential use in microelectronic and integrated-circuit technologies [48].

The imaginary part of the dielectric function, $\varepsilon_2(\omega)$, reflects the material's absorption characteristics associated with electronic transitions from the valence band to the conduction band. The $\varepsilon_2(\omega)$ spectra for X_2SnI_4 ($\text{X} = \text{GUA}, \text{DMA}, \text{MA}$) at 0 and 8 GPa are presented in Figure 5F, S5f and S6f. At ambient pressure, the maximum $\varepsilon_2(\omega)$ peaks occur at 2.67 eV, 2.57 eV, and 2.11 eV for GUA_2SnI_4 , DMA_2SnI_4 , and MA_2SnI_4 , respectively. With increasing hydrostatic pressure, these peaks intensify and shift toward higher photon

energies, indicating enhanced optical absorption due to pressure-induced modifications in the electronic structure.

3. Simulation Details

The simulation uses a fully unconstrained 3D triclinic lattice with lattice parameters $a = 6.242549 \text{ \AA}$, $b = 6.09115 \text{ \AA}$, and $c = 27.519767 \text{ \AA}$, and lattice angles $\alpha = 89.89209^\circ$, $\beta = 91.97904^\circ$, and $\gamma = 91.65721^\circ$. A CASTEP geometry optimization calculation was performed with medium-quality settings using the GGA-PBE exchange–correlation functional without TS dispersion correction. Spin polarization was enabled with the formal spin used as the initial configuration. The calculation employed a 500 eV plane-wave energy cutoff, medium SCF tolerance and convergence settings, a $2 \times 2 \times 1$ Monkhorst–Pack k-point mesh, and norm-conserving pseudopotentials with Koelling–Harmon relativistic treatment. SCF settings included a tolerance of $2.0 \times 10^{-6} \text{ eV/atom}$, a maximum of 100 SCF cycles, a convergence window of 3, an all-bands/EDFT minimizer, density mixing with a charge of 0.5 and spin of 2.0, and fixed orbital occupancy; no dipole correction was applied. For accurate electronic structure analysis, the band gap at zero pressure was calculated using the hybrid functional HSE06, while the band-gap variation under applied pressure was evaluated using the GGA-PBE functional. HSE06 was chosen for ambient pressure due to its higher accuracy in predicting band gaps, while PBE-GGA was used for pressure-dependent calculations because it is computationally more efficient, especially for large-scale simulations [28,49].

4. Conclusions

First-principles calculations on the 2D Ruddlesden–Popper iodide perovskites $A_2\text{SnI}_4$ ($A = \text{GUA}^+$, DMA^+ , MA^+) show that all three compositions are direct-gap semiconductors at ambient conditions, with HSE06 band gaps of 2.85 eV, 2.98 eV, and 2.25 eV, respectively. Although they share the same layered SnI_6 framework, their electronic responses to hydrostatic pressure differ significantly. GUA_2SnI_4 shows the strongest pressure tunability, with its band gap decreasing from 2.31 eV at 0 GPa to 0.59 eV at 8 GPa and experiencing a direct–indirect transition near 2 GPa. MA_2SnI_4 follows a similar trend, narrowing from 1.88 eV to 0.34 eV over the same pressure range, while DMA_2SnI_4 remains comparatively insensitive, stabilizing near 1.70 eV above 4 GPa. Corresponding shifts in dielectric, loss, and absorption spectra reflect these contrasting behaviors, with GUA_2SnI_4 showing the most noticeable optical changes under increasing hydrostatic pressure. Collectively, these results indicate that GUA_2SnI_4 , DMA_2SnI_4 , and MA_2SnI_4 define three distinct regimes of optoelectronic tunability, ranging from strongly pressure-responsive to nearly pressure-invariant, providing a versatile materials platform for designing lead-free absorber layers. The clear distinction among the three perovskite materials guides the selection of specific A-site cations to optimize the spectral response and operational characteristics of tin-based 2D RP perovskites for photovoltaic applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics14030073/s1>, Figure S1: HSE06-calculated projected density of states (PDOS) of the 2D GUA_2SnI_4 monolayer with the Fermi level set at 0 eV: (A) C atom, (B) H atom, (C) N atom, (D) I atom, and (E) Sn atom. Figure S2: HSE06-calculated PDOS of the 2D MA_2SnI_4 monolayer with the Fermi level set at 0 eV: (A) C atom, (B) H atom, (C) N atom, (D) I atom, and (E) Sn atom. Figure S3: GGA-PBE band gap of GUA_2SnI_4 under hydrostatic pressure: (A) 0 GPa, (B) 2 GPa, (C) 4 GPa, (D) 6 GPa, and (E) 8 GPa. Figure S4: GGA-PBE band gap of MA_2SnI_4 under hydrostatic pressure: (A) 0 GPa, (B) 2 GPa, (C) 4 GPa, (D) 6 GPa, and (E) 8 GPa. Figure S5: The calculated (A) absorption; (B) loss function; (C) reflectivity; (D) refractive index; (E) conductivity; and (F) dielectric function for 2D GUA_2SnI_4 under hydrostatic pressure. Figure S6:

The calculated (A) absorption; (B) loss function; (C) reflectivity; (D) refractive index; (E) conductivity; and (F) dielectric function for 2D MA₂SnI₄ under hydrostatic pressure.

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