

Lead-free Cs_2MH_6 ($\text{M} = \text{Ge}, \text{Sn}$) vacancy-ordered double perovskites for optoelectronic applications: a first-principles study

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Abstract

Lead-free vacancy-ordered double perovskite hydrides are gaining attention as environmentally friendly materials for next-generation optoelectronic applications. In this work, first-principles density functional theory (DFT) calculations are employed to systematically investigate the structural, elastic, electronic, optical, and thermodynamic properties of cubic Cs_2GeH_6 and Cs_2SnH_6 crystallizing in the antiperovskite-type $\text{Fm}\bar{3}\text{m}$ structure. Structural optimization yields lattice constants of 8.620 Å and 8.990 Å, respectively, while negative formation energies confirm thermodynamic stability. Phonon dispersion analysis shows no imaginary modes, establishing dynamical stability. Elastic constants satisfy the Born criteria, indicating mechanically robust lattices with near-isotropic behavior in Cs_2GeH_6 and moderate anisotropy in Cs_2SnH_6 . Electronic structure calculations reveal that both compounds are direct band-gap semiconductors, with band gaps of 1.60 eV (Cs_2GeH_6) and 1.80 eV (Cs_2SnH_6). Density-of-states and charge-density analyses indicate mixed ionic-covalent bonding, dominated by strong Cs–H ionic interactions and covalent M–H bonding within isolated $[\text{MH}_6]^{2-}$ octahedra. Optical calculations show an enhanced dielectric response and high absorption coefficients in the visible spectrum. Thermodynamic analysis indicates a stiffer lattice and higher Debye temperature for Cs_2GeH_6 . These findings suggest that Cs_2GeH_6 and Cs_2SnH_6 are mechanically robust, thermally stable, and optically tunable lead-free perovskite hydrides, making them promising candidates for photovoltaic optoelectronic applications.

Keywords Vacancy-ordered double perovskites · Cs_2MH_6 ($\text{M} = \text{Ge}, \text{Sn}$) · Density functional theory (DFT) · Direct band gap semiconductors · Phonon dispersion · Stability optoelectronic properties

Introduction

The global energy system is currently undergoing a significant transformation driven by the steadily rising demand for energy worldwide. This increase in consumption has intensified the need to reconsider how energy is generated, transmitted, stored, and ultimately utilized in a sustainable manner¹. Within this context, solar energy conversion has attracted considerable interest, largely because solar energy is abundant, environmentally benign,

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and capable of supporting long-term energy requirements^{2,3}. The performance of solar cells and optoelectronic devices is closely linked to the properties of the active materials employed. In particular, efficient absorption of visible light, combined with adequate structural and thermodynamic stability, is essential for reliable device operation^{4,5}. For this reason, extensive research efforts have been devoted to identifying semiconducting materials with band gaps in the optimal range of approximately 1.5–2.0 eV, which is considered ideal for photovoltaic and photoactive applications⁶. In recent years, perovskite materials have emerged as one of the most promising classes of semiconductors due to their remarkable optoelectronic performance, structural versatility, and ease of compositional engineering^{7,8}. The characteristic ABX₃ perovskite framework accommodates a wide range of elemental substitutions at the A, B, and X sites. This flexibility enables systematic tuning of key material properties, including the band gap, stability, and charge transport behavior, making perovskites highly attractive for next-generation optoelectronic technologies⁹.

Double perovskite (DP) semiconductors have gained increasing attention in recent years because of their strong potential for optoelectronic applications^{10,11}. A key advantage of these materials lies in their pronounced structural and compositional flexibility, which allows their electronic properties to be tailored through targeted elemental substitution. As a result, many double perovskites exhibit favorable optoelectronic characteristics, including high charge-carrier mobility, strong absorption in the visible region, efficient carrier transport, tunable band gaps, and relatively low effective masses^{12,13}. These features make DP semiconductors particularly attractive for a broad range of electronic and photonic devices. Consequently, perovskite-based semiconductors are now central to several modern technologies, such as light-emitting diodes, photodetectors, and sensing platforms, as well as emerging information-processing devices. Beyond conventional optoelectronics, their influence is expanding into wider application areas, including communication systems, transportation technologies, and healthcare-related devices, highlighting their growing technological relevance¹⁴.

Optoelectronic materials are designed to enable efficient conversion between optical and electrical signals, which is essential for modern energy and information technologies. Within this framework, organic–inorganic hybrid perovskites have attracted substantial interest because of their high photovoltaic efficiencies and their demonstrated potential in devices such as light-emitting diodes and transistors^{15,16}. A notable example of this progress is the rapid increase in the power conversion efficiency of perovskite solar cells, which has risen from approximately 3.8% to 25.5% in just over a decade⁴. Despite these impressive performance gains, many of the most efficient halide perovskites rely on lead as a key component, giving rise to serious concerns regarding toxicity and environmental sustainability^{17,18}. In response, significant research efforts have been directed toward the development of lead-free double perovskites. These materials offer greater compositional flexibility, competitive optoelectronic performance, and improved environmental compatibility, making them attractive candidates for solar cell and optoelectronic applications^{19–21}. From an environmental perspective, the replacement of hazardous lead with benign alternatives is a central design goal. One commonly explored approach involves substituting Pb with elements from the same group of the periodic table, particularly tin (Sn) and germanium (Ge), which share similar valence configurations^{22,23}. However, solar cell devices based on Sn- and Ge-containing perovskites have, to date, generally exhibited lower power conversion efficiencies than their lead-based counterparts, highlighting the need for further materials optimization²⁴.

Vacancy-ordered double perovskites with the general formula A₂BX₆ have emerged as an important subclass of perovskite materials because of their inherent structural stability and tunable electronic behavior. These compounds are characterized by an ordered arrangement of vacancies that strongly influences their electronic structure and lattice dynamics. In a representative study, Maham M. S. Karim et al. demonstrated that Cs₂SnX₆ (X = Cl, Br, I) compounds crystallizing in the cubic *Fm* $\bar{3}$ *m* phase exhibit composition-dependent optical band gaps, pronounced octahedral distortions, and distinct vibrational features. Their conclusions were supported by a combination of experimental measurements and first-principles calculations, highlighting the sensitivity of the optoelectronic properties to halide substitution²⁵. These findings highlight the strong sensitivity of electronic and vibrational properties to the local coordination of the BX₆ octahedra. Despite extensive investigations of halide-based A₂BX₆

systems, their hydride counterparts, such as Cs_2SnH_6 and Cs_2GeH_6 , remain largely unexplored. Recent experimental advances have further enhanced the technological relevance of vacancy-ordered Cs_2SnX_6 ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) perovskites. Perovskite nanocrystals have been encapsulated in more stable and environmentally safe materials, such as metal oxides (such as AlO_x and TiO_2)²⁶, polymers²⁷, silica²⁸, and metal–organic frameworks (MOFs)²⁹, which act as protective shells for the perovskite nanocrystals in order to reduce stability and toxicity concerns. In particular, the epitaxial growth of Cs_2SnX_6 shells on all-inorganic CsPbX_3 nanocrystals has enabled the formation of stable core–shell heterostructures with tunable type-I and type-II band alignments, exhibiting excellent optical performance, efficient charge transport, and strong resistance to moisture, light, and air exposure³⁰. These observations confirm that Cs_2Sn -based A_2BX_6 perovskites are structurally stable and functionally versatile materials. At the same time, they emphasize the importance of extending existing studies beyond halide systems in order to gain deeper insight into the intrinsic structural, electronic, and vibrational properties of this class of compounds. Determination of the electronic band structures and optical spectra of semiconductor electronics, photovoltaics, and optoelectronic devices are particularly important for technological applications. Hydride research is fascinating from a fundamental perspective and appealing in terms of potential technological uses.

Accurate theoretical predictions of perovskite properties depend strongly on the choice of exchange–correlation (XC) functional within density functional theory (DFT)³¹. Among the available approaches, the local density approximation (LDA) and the generalized gradient approximation (GGA) remain the most widely employed because they offer a practical balance between accuracy and computational cost. LDA is known to overbind atoms, often resulting in underestimated lattice constants and overestimated cohesive energies, whereas GGA incorporates density gradients, leading to improved structural parameters and energetics for many solid-state systems^{32–34}. Comparative studies on oxide and halide perovskites, including those reported by García-Fernández et al.³⁵, and Borlido et al.³⁶ show that GGA—particularly in the form of the PBE functional provides equilibrium geometries that are generally in better agreement with experimental data. However, both LDA and GGA are found to systematically underestimate electronic band gaps. These findings highlight that careful selection of the XC functional is essential to achieve a meaningful compromise between structural accuracy and reliable electronic property predictions in perovskite modeling.

Recently, lead-free hydride perovskites have been identified as environmentally stable semiconductors with suitable band gaps of approximately visible range, placing them within the optimal range for visible-light absorption^{11,37–39}. A detailed understanding of their structural and electronic behavior under different XC approximations can therefore provide critical insights into the design and optimization of high-performance, sustainable perovskite-based devices.

In this work Density functional theory (DFT) calculations were performed using the plane-wave pseudopotential method as implemented in the Cambridge Serial Total Energy Package (CASTEP) within the Materials Studio framework to systematically examine the Optoelectronic properties of hydride perovskites Cs_2GeH_6 and Cs_2SnH_6 . However, to the best of our knowledge, a comprehensive first-principles density functional theory (DFT) investigation of the structural, elastic, electronic, thermodynamic and optical properties of the hydride perovskites Cs_2GeH_6 and Cs_2SnH_6 has not yet been reported.

The remainder of the paper is organized as follows: Section "[Computational details](#)" outlines the computational methodology, Section "[Results and discussion](#)" presents and discusses the structural, elastic, electronic, optical, and Thermodynamic results, and Sect. 4 summarize the main conclusions.

Computational details

First-principles calculations were carried out using the CASTEP code within the framework of Density Functional Theory (DFT) as implemented in Materials Studio 2020⁴⁰. The exchange–correlation interactions were described using the Generalized Gradient Approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional^{32,41}, while ion–electron interactions were treated using ultrasoft pseudopotentials. A scalar-relativistic

Koelling–Harmon approach was applied to accurately describe the heavy Cs atoms. The valence electron configurations considered were H ($1s^1$), Ge ($4s^24p^2$), Sn ($5s^25p^2$), and Cs ($5s^25p^66s^1$).

The crystal structures of Cs_2GeH_6 and Cs_2SnH_6 were modeled in the cubic $Fm\bar{3}m$ (No. 225) space group with lattice parameters of 8.620 Å and 8.990 Å, respectively. A plane-wave energy cutoff of 380 eV and a $4 \times 4 \times 4$ Monkhorst–Pack k-point mesh were employed^{42,43}. The choice of these plane-wave and sampling grid parameters was strictly validated through systematic pre-calculation convergence tests, confirming that further increases in either the cutoff threshold or k-mesh density produce total energy fluctuations below 0.5 meV/atom and maintain band gap stability to within 0.01 eV. Structural optimization was performed using the BFGS algorithm with convergence criteria of 1.0×10^{-5} eV/atom for total energy, 0.03 eV/Å for forces, 0.05 GPa for stress, and 1.0×10^{-3} Å for atomic displacements.

Phonon properties were calculated using Density Functional Perturbation Theory (DFPT)^{44,45}. Born effective charges were computed to include long-range electrostatic interactions, enabling the evaluation of non-analytic corrections and LO–TO splitting at the Γ point. Phonon dispersion relations along the high-symmetry path (G – F – Q – Z – G) and phonon density of states were analyzed to assess the dynamical stability of the compounds.

Results and discussion

Structural properties and stability

The structural properties of Cs_2GeH_6 and Cs_2SnH_6 were examined through full geometry optimization of both the unit cell parameters and internal atomic positions (Fig. 1). The calculations confirm that both compounds are stable in the cubic antiperovskite-type structure, also referred to as the $K_2\text{PtCl}_6$ -type or ordered vacancy double perovskite structure, crystallizing in the $Fm\bar{3}m$ (No. 225) space group.

In this crystal structure, the Ge/Sn atoms occupy the $4a$ Wyckoff position (0,0,0), while the Cs atoms reside at the $8c$ site (0.25,0.25,0.25). The hydrogen atoms are located at the $24e$ Wyckoff position ($x,0,0$). The resulting framework consists of isolated $[\text{MH}_6]^{2-}$ octahedra positioned at the corners and face centers of the cubic unit cell,

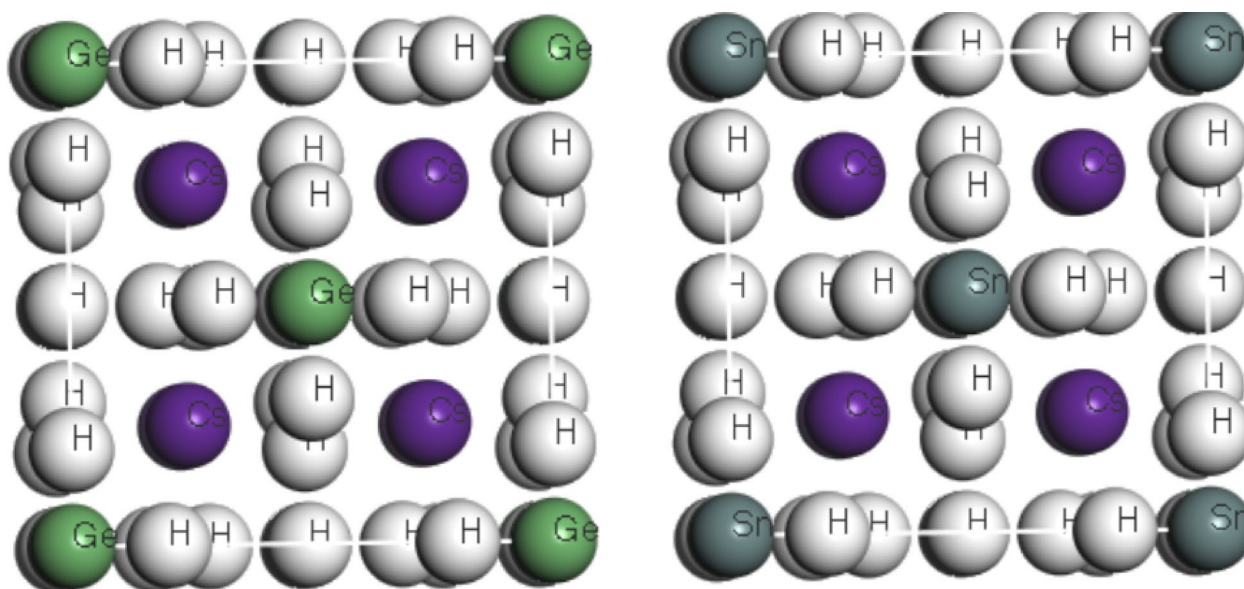


Fig. 1 Optimized crystal structure and modeling framework of vacancy-ordered double perovskite hydrides Cs_2GeH_6 and Cs_2SnH_6

with the Cs atoms forming a three-dimensional cubic sublattice that provides structural stabilization. The structure consists of isolated $[MH_6]^{2-}$ octahedra embedded in a Cs -based cubic lattice. Unlike ABX_3 perovskites, the vacancy-ordered A_2BX_6 framework avoids corner-sharing connectivity, thereby eliminating under-coordinated atoms and dangling bonds. Charge neutrality is fully maintained ($2Cs^+ + M^{4+} + 6H^- = 0$), and the fully coordinated M^{4+} centers form stable closed-shell configurations, which suppress the formation of mid-gap defect states.

The optimized structural parameters are summarized in Table 1. The calculated lattice constants are 8.620 Å for Cs_2GeH_6 and 8.990 Å for Cs_2SnH_6 . The corresponding unit cell volumes increase from 640.504 Å³ to 726.573 Å³ upon replacing Ge with the larger Sn atom. This expansion reflects the size difference between the two metal cations and follows the expected periodic trend. These results are in excellent agreement with previous theoretical studies by Boudrifa, O., et al.⁴³ and Luo et al.⁴⁴, who reported that lattice parameters in A_2MH_6 complex hydrides scale systematically with the ionic radius of the central M cation.

A key structural feature of these materials is the $M-H$ bond length within the $[MH_6]^{2-}$ octahedral unit. After structural relaxation, the internal hydrogen positional parameter (x) was found to be 0.21 for Cs_2GeH_6 and 0.20 for Cs_2SnH_6 , corresponding to bond lengths of 1.81 Å and 1.80 Å, respectively. These results confirm the stability of the octahedral coordination and are in good agreement with previously reported structural benchmarks⁴⁶.

Before examining the electronic, optical, and other physical properties, a comprehensive evaluation of structural stability was performed, considering thermodynamic, mechanical, and dynamical stability criteria.

Thermodynamic stability

The thermodynamic stability of the investigated compounds was assessed by calculating the formation energy ΔH_f , which provides a measure of energetic favorability relative to the constituent elements. The formation energy per atom was computed using the following expression:

$$\Delta H_f = \frac{E(Cs_2MH_6) - 2E(Cs) - E(M) - 6E(H)}{9}, \tag{1}$$

where ΔH_f denotes the formation energy per atom, $E(Cs_2MH_6)$ is the total energy of the fully optimized compound, and $E(Cs)$, $E(M)$, and $E(H)$ represent the average total energies of the constituent elements in their respective reference states. The denominator corresponds to the total number of atoms in the formula unit. As summarized in Table 1, the calculated formation energies are −0.62 eV/atom for Cs_2GeH_6 and −0.58 eV/atom for Cs_2SnH_6 . The negative values indicate that both compounds are thermodynamically stable and energetically favorable with respect to elemental decomposition. These results are consistent with previously reported theoretical studies on A_2MH_6 vacancy-ordered perovskites⁴⁷.

Table 1 Optimized lattice constant (a), unit cell volume (V), internal hydrogen coordinate (x), metal–hydrogen bond length (M–H), and formation energy (ΔH_f) of ordered vacancy double perovskite hydrides.

Compounds	Data source	a (Å)	V (Å ³)	M–H (Å)	ΔH_f (eV/atom)
Cs_2GeH_6	This work	8.620	640.504	1.81	−0.62
Cs_2SnH_6	This work	8.990	726.573	1.80	−0.58
Ba_2BeH_6	⁴⁴	7.577	435.023	1.64	−0.75
Ba_2CaH_6	⁴⁴	8.102	531.921	2.13	−0.57
Ba_2MgH_6	⁴⁴	7.915	495.765	1.92	−0.74
Ca_2BeH_6	⁴⁴	6.757	308.527	1.60	−0.84
Sr_2MgH_6	⁴⁴	7.511	423.737	1.90	−0.75

Reference data are taken from Luo et al.⁴⁴ (Nanomaterials 2025, 15, 1339).

Dynamical stability

Phonon dispersion analysis is a key method for assessing the dynamical stability of crystalline materials, as it provides direct information about lattice vibrations and interatomic interactions. The absence of imaginary phonon frequencies throughout the Brillouin zone is generally taken as evidence of dynamical stability, whereas the presence of such modes indicates structural instabilities or possible phase transitions. The Cs_2MH_6 ($M = \text{Ge}, \text{Sn}$) compounds contain nine atoms per primitive cell, giving rise to a total of 27 phonon branches, which include three acoustic modes and 24 optical modes.

The calculated phonon dispersion curves (Fig. 2) along the high-symmetry k-points of the Brillouin zone ($\text{G} - \text{F} - \text{Q} - \text{Z} - \text{G}$) are shown in Fig. 1. A key observation is the complete absence of imaginary (negative) frequencies for both Cs_2GeH_6 and Cs_2SnH_6 , indicating that these materials are dynamically stable. The absence of imaginary phonon modes across the entire Brillouin zone confirms that both compounds reside at a true local minimum on the potential energy surface. This means that all phonon modes correspond to positive curvature, and there are no lattice vibration directions that can lower the total energy. In contrast, imaginary modes would indicate structural instabilities leading to spontaneous distortions such as symmetry breaking or phase transitions. Since no such unstable modes are present, the cubic phase is dynamically stable and any possible phase transition would require overcoming a finite energy barrier, which is not accessible under low-temperature conditions.

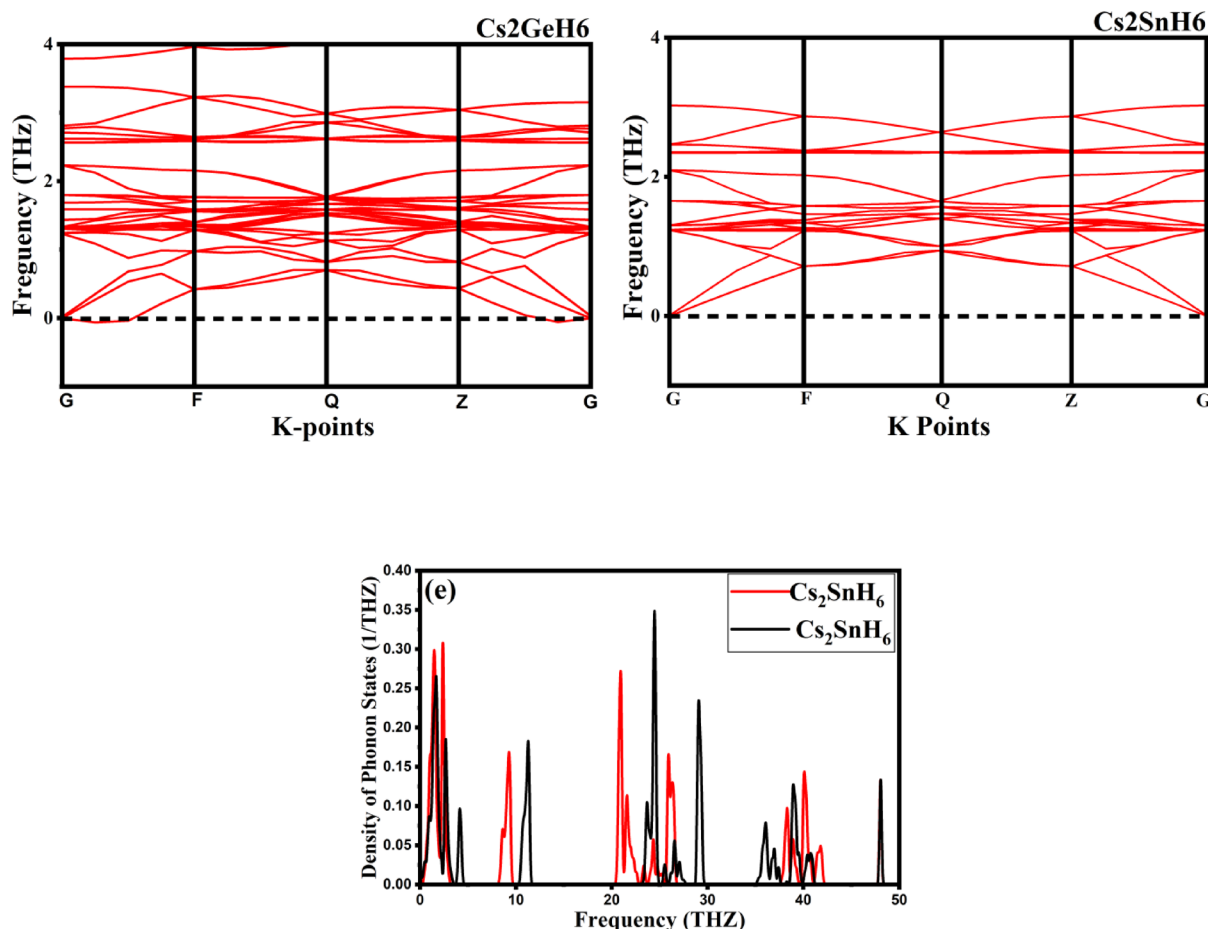


Fig. 2 Phonon dispersion curves and DOS of Cs_2GeH_6 and Cs_2SnH_6 .

The dispersion curves also reveal a clear separation between the low-frequency acoustic and optical modes, dominated by the heavier Cs and Ge/Sn atoms, and the high-frequency optical modes associated with vibrations of the lighter hydrogen atoms within the $[\text{MH}_6]^{2-}$ octahedra.

The absence of imaginary modes confirms that both compounds correspond to true local minima on the potential energy surface, ensuring their long-term structural stability. These results further validate the reliability of the PBE-GGA functional employed in this study and support the potential use of these materials in energy storage and optoelectronic applications⁴⁶.

Mechanical stability

Predicting the mechanical behavior of Cs_2SnH_6 and Cs_2GeH_6 is essential for evaluating their suitability in optoelectronic applications. Elastic parameters provide insight into how these A_2MH_6 ($\text{M}=\text{Ge}, \text{Sn}$) vacancy-ordered double perovskites respond to stress, which can influence both electronic and optical performance. The mechanical properties were calculated using the GGA-PBE functional, which has been widely validated for predicting the elastic behavior of crystalline materials, while the HSE06 hybrid functional was employed only for the electronic and optical property calculations. Using the calculated elastic constants, key mechanical parameters including elastic anisotropy (A), bulk modulus (B), shear modulus (G), Young's modulus (E), Poisson's ratio (ν), and Vickers hardness (H) were determined using the following Elastic Property Equations:^{48,49}.

Elastic Anisotropy:

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (2)$$

Bulk Modulus:

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

Voigt Shear Modulus:

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

Reuss Shear Modulus:

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

Average Shear Modulus:

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

Young's Modulus:

$$E = \frac{9BG}{3B + G} \quad (7)$$

Poisson's Ratio:

$$\nu = \frac{3B - 2G}{2(3B + G)} \quad (8)$$

The computed mechanical parameters are summarized in Table 2. Cs_2GeH_6 exhibits higher elastic stiffness than Cs_2SnH_6 , with $B=10.08$ GPa vs. 3.75 GPa, $G=11.42$ GPa vs. 6.74 GPa, and $E=24.86$ GPa vs. 12.65 GPa. This

Table 2 Elastic and thermal properties of Cs₂SnH₆ and Cs₂GeH₆.

Material	Cs ₂ SnH ₆	Cs ₂ GeH ₆
B (GPa)	3.748	10.079
G (GPa)	6.743	11.417
E (GPa)	12.646	24.862
N	−0.062	0.089
E_min (GPa)	11.045	24.532
E_max (GPa)	14.498	24.670
A	1.313	0.00086
H (GPa)	6.928	5.944
T (K)	549–567	567–580

indicates that Cs₂GeH₆ is mechanically more rigid, while the softer Cs₂SnH₆ can better accommodate strain without fracture, which is beneficial for thin-film optoelectronic applications.

The calculated Poisson’s ratio for Cs₂SnH₆ is −0.062, indicating a weak auxetic tendency. This behavior can be attributed to the vacancy-ordered zero-dimensional (0D) structure composed of isolated [SnH₆]^{2−} octahedra embedded within a compliant Cs⁺ ionic matrix. The absence of a continuous corner-sharing network allows enhanced local structural flexibility under applied strain, which can lead to unconventional transverse strain response. However, the small magnitude of the negative value suggests that the auxetic effect is weak. In contrast, Cs₂GeH₆ exhibits a small positive Poisson’s ratio (0.089), consistent with conventional elastic behavior.

Vickers hardness, calculated via Chen’s model⁵⁰ is 6.93 GPa for Cs₂SnH₆ and 5.94 GPa for Cs₂GeH₆, confirming sufficient mechanical robustness for device fabrication. The melting points, estimated from elastic constants using the relation⁵¹:

$$T_m = [553 + 5.911 \times C_{12}] \pm 300K \tag{9}$$

are approximately 549–567 K for Cs₂SnH₆ and 567–580 K for Cs₂GeH₆, suggesting thermal stability suitable for optoelectronic processing.

When compared with previously reported A₂MH₆ perovskites (e.g., Ca₂BeH₆ and Ba₂MgH₆), which exhibit B/G ratios ranging from 1.11 to 1.42^{49,50}, Cs₂SnH₆ and Cs₂GeH₆ are moderately softer and show lower B/G ratios of 0.56 and 0.88, respectively. According to the Pugh criterion, these values place both hydrides in the brittle regime (B/G < 1.75). However, their relatively low Young’s moduli (E = 12.65 GPa for Cs₂SnH₆ and 24.86 GPa for Cs₂GeH₆) indicate high mechanical compliance.

In flexible optoelectronic applications, a low Young’s modulus reduces internal bending stress ($\sigma = E \cdot \epsilon$), thereby suppressing crack formation under applied strain in thin-film configurations. This combination of mechanical stability, low stiffness, and near-isotropic behavior makes these materials promising candidates for flexible optoelectronic devices where strain tolerance and stable optical response are essential.

The spatial distributions of Young’s modulus, shear modulus, and Poisson’s ratio, obtained using ELATE^{52–54} are shown in Fig. 3a–c for Cs₂SnH₆ and Fig. 4a–c for Cs₂GeH₆. These plots demonstrate quasi-isotropic behavior with minor directional variations, further supporting uniform electronic and optical response in both thin-film and bulk configurations.

Since Cs₂SnH₆ and Cs₂GeH₆ have been confirmed to be thermodynamically, dynamically, and mechanically stable, we now turn our attention to their electronic, optical, and thermodynamic properties to assess their suitability for optoelectronic application.

Electronic properties

The electronic properties of Cs₂GeH₆ and Cs₂SnH₆ were examined through a systematic analysis of their electronic band structures⁵⁵, total density of states (TDOS), and partial density of states (PDOS) to evaluate their potential for optoelectronic and photovoltaic applications. The computed band structures of Cs₂GeH₆ and Cs₂SnH₆ along

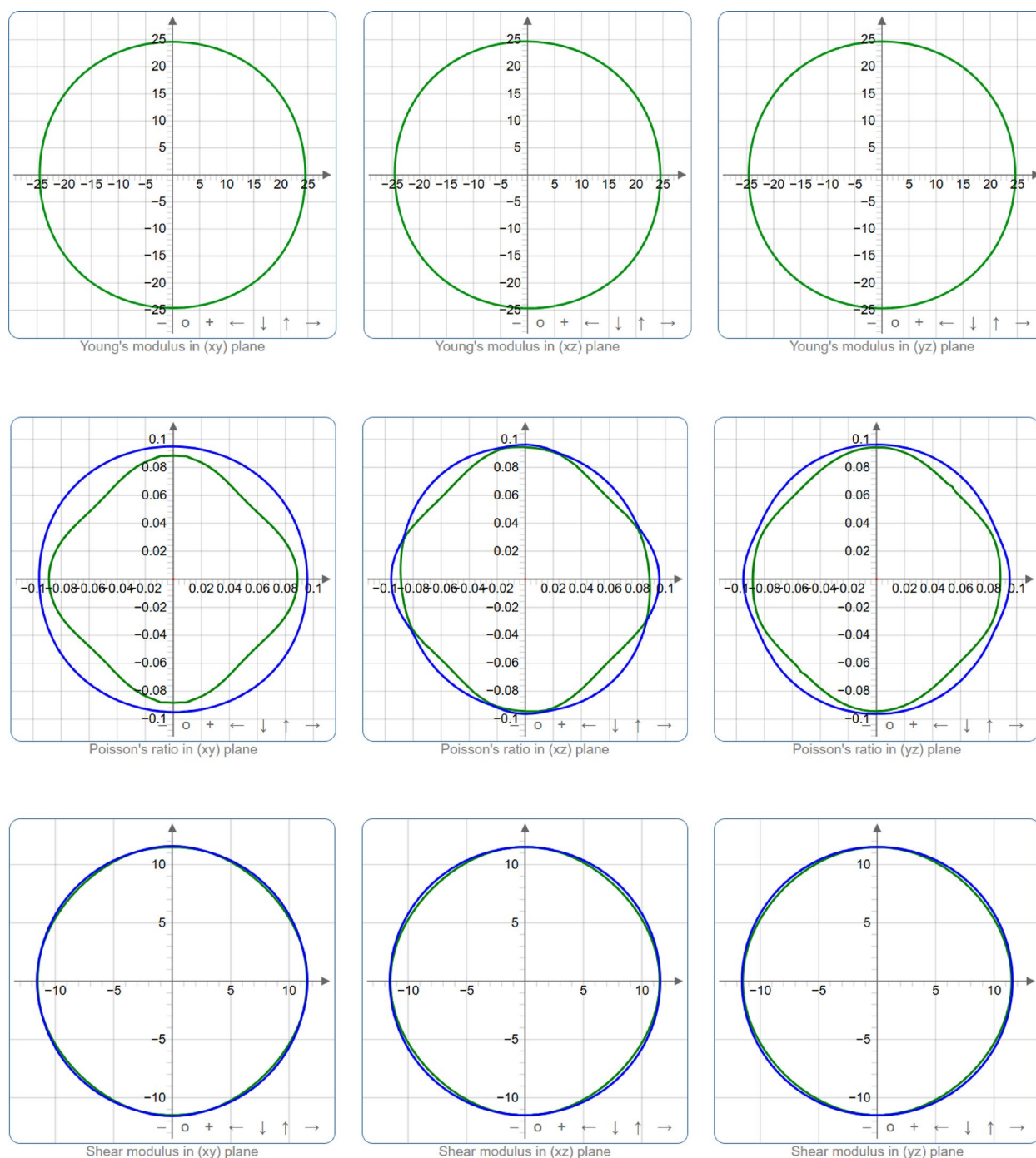
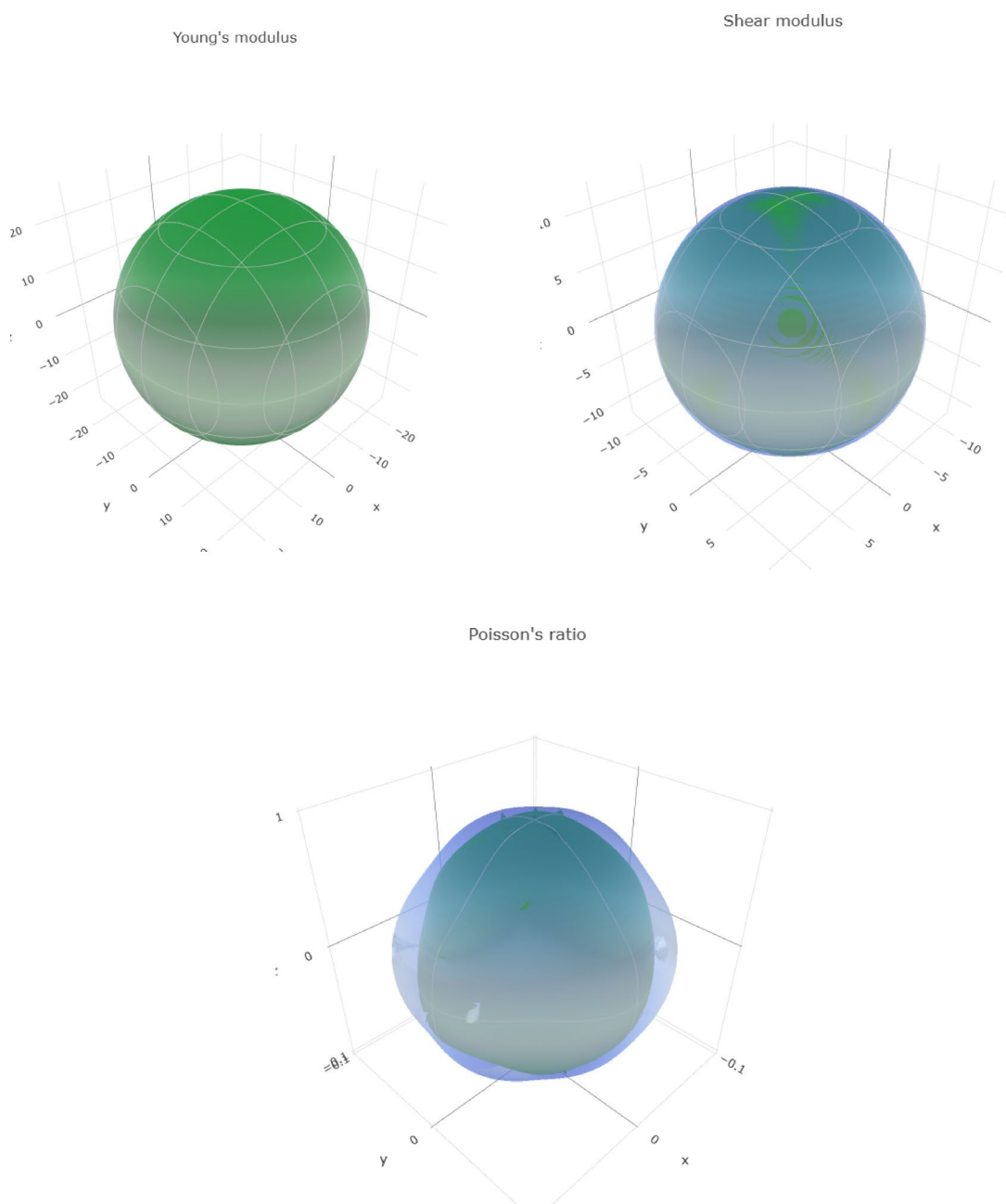


Fig. 3 Spatial distributions of (a) Young's modulus (E), (b) shear modulus (G), and (c) Poisson's ratio (ν) for Cs_2SnH_6 , shown in both 2D and 3D representations, visualized using ELATE, illustrating quasi-isotropic elastic behavior with minor directional variations.

the high-symmetry directions of the Brillouin zone^{56,57} are presented in Fig. 5, obtained using both the generalized gradient approximation (GGA-PBE) and the local density approximation (LDA). The horizontal dashed line at 0 eV denotes the Fermi energy. In both compounds, the valence band states are entirely located below the Fermi level, while the conduction band states appear above it, with no band crossing at the Fermi level, confirming the non-metallic and intrinsic semiconducting nature of these materials. The valence band maximum

**Fig. 3** (continued)

and conduction band minimum are found at the Γ symmetry point for both compounds, indicating that Cs_2GeH_6 and Cs_2SnH_6 possess direct band gaps, which is favorable for efficient optical transitions without momentum change. Exchange–correlation phenomena primarily account for the observed discrepancies between the GGA and the LDA⁵⁸. The calculated band gap values show a clear dependence on the exchange–correlation functional. Within the GGA-PBE approximation, the direct band gaps are approximately 1.60 eV for Cs_2GeH_6 and 1.80 eV for Cs_2SnH_6 , placing both materials in the visible-light energy range. In contrast, the LDA approach yields smaller band gaps of about 1.39 eV and 1.50 eV, respectively, consistent with the well-known tendency of LDA to underestimate band gaps due to its simplified treatment of exchange–correlation effects. Furthermore, the HSE06 hybrid functional provides improved band gap values of 2.41 eV for Cs_2GeH_6 and 2.18 eV for Cs_2SnH_6 , offering a

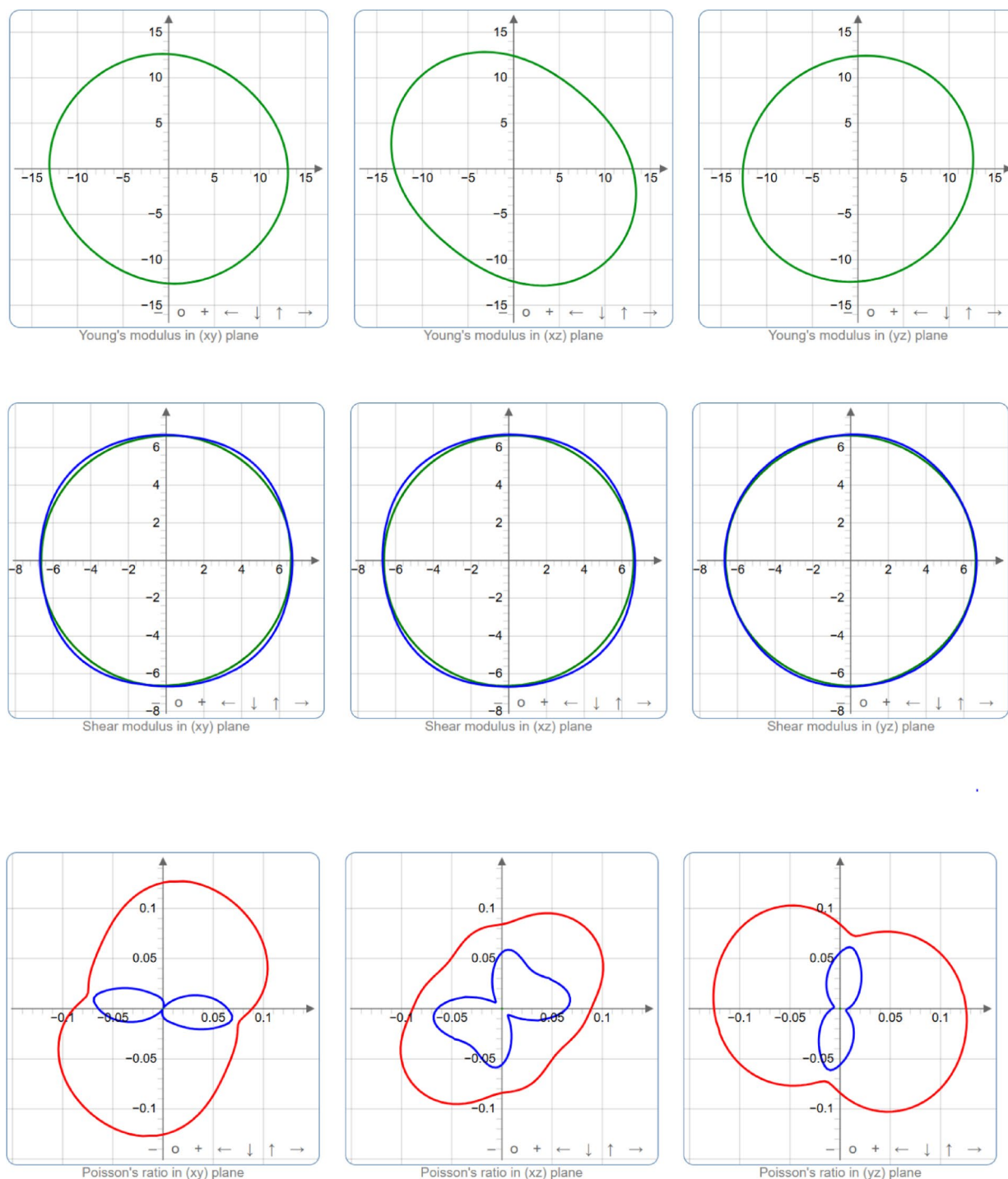
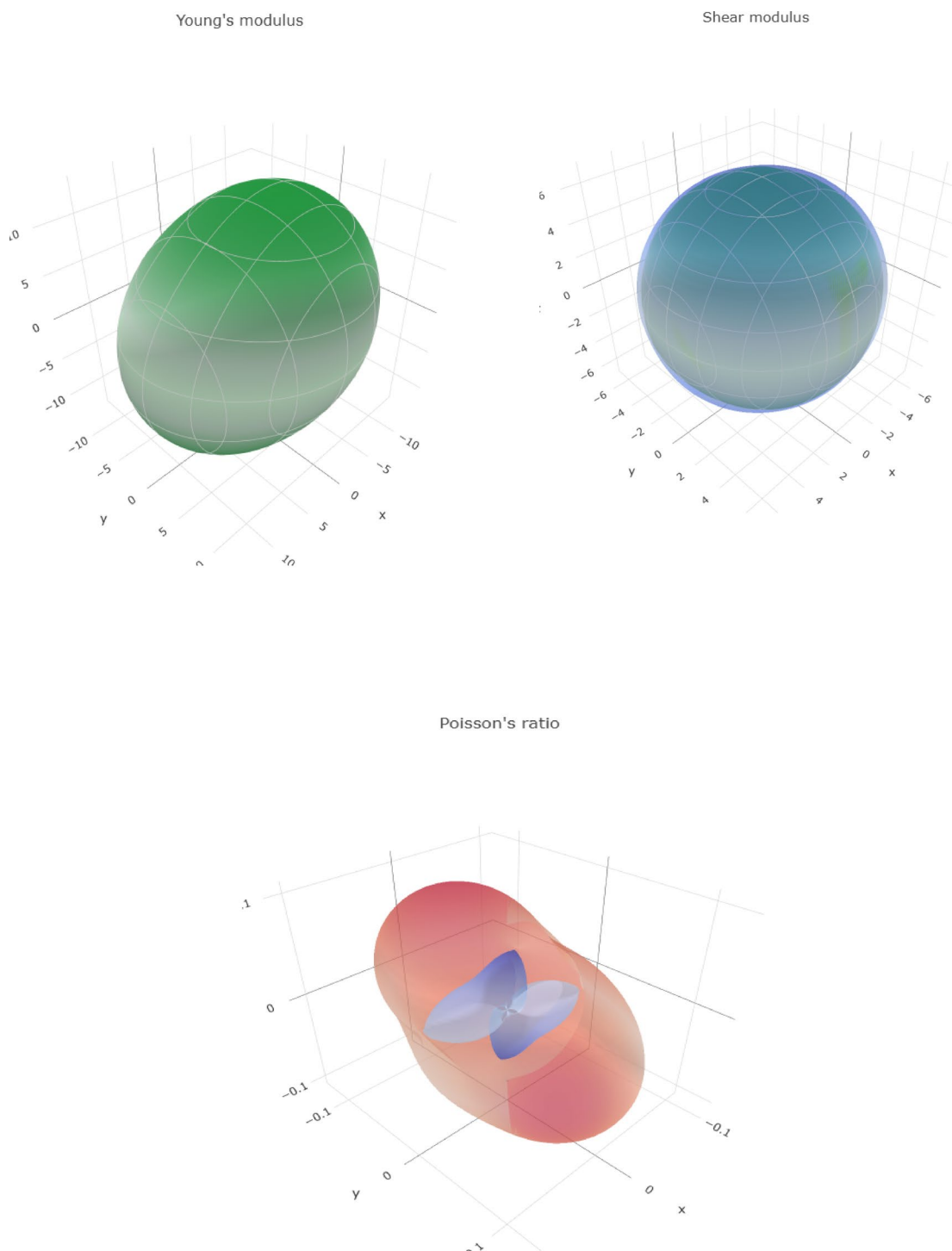


Fig. 4 Spatial distributions of **(a)** Young's modulus (E), **(b)** shear modulus (G), and **(c)** Poisson's ratio (ν) for Cs_2GeH_6 shown in both 2D and 3D representations, calculated and visualized using ELATE, illustrating near-isotropic elastic behavior with minimal directional variation

**Fig. 4** (continued)

more accurate description of the electronic structure^{59,60}. Compared to LDA, the PBE functional systematically predicts wider band gaps, leading to a relative blue shift of the optical absorption edge. This behavior suggests that Cs_2SnH_6 exhibits a slightly larger band gap than Cs_2GeH_6 , indicating higher-energy optical absorption, while both materials demonstrate electronic characteristics that make them promising candidates for lead-free optoelectronic and photovoltaic devices.

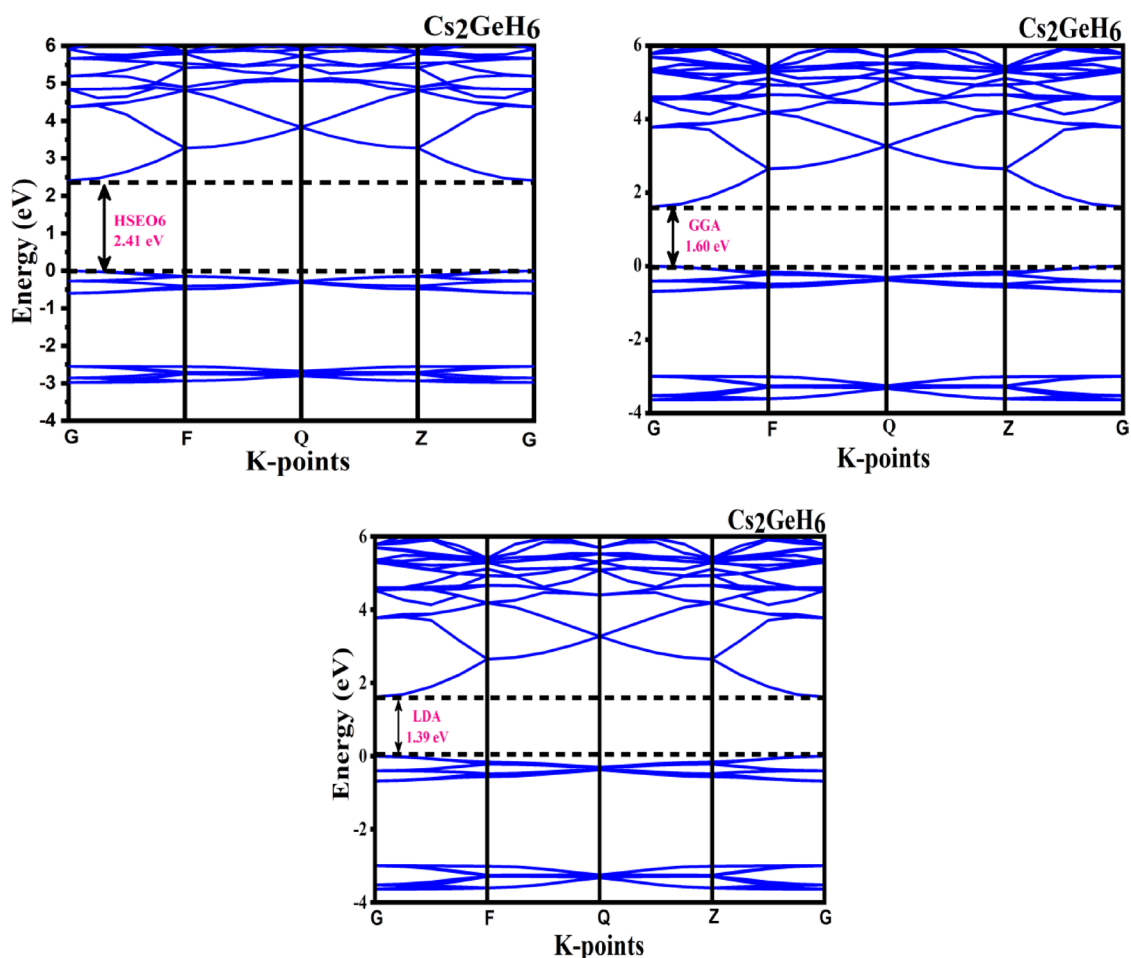


Fig. 5 Band structure of Cs_2GeH_6 and Cs_2SnH_6 with Hybrid function, GGA and LDA exchange correlation functions respectively.

Figure 6 displays the TDOS and PDOS for Cs_2GeH_6 and Cs_2SnH_6 , as calculated using the GGA-PBE and LDA functionals. The energy scale is referenced to the valence band maximum (VBM), which is set at 0 eV. The region above this value represents the electronic band gap. For both compounds, the valence band ranges from approximately -9 eV to the Fermi level, while the conduction band starts above the band gap and extends to higher energies. The TDOS in the valence band exhibits significant intensity peaks, indicating a high density of occupied electronic states. A pronounced, slender peak in the deep valence region, approximately between -9 and -6 eV, predominantly originates from H-1s states, with slight contributions from Ge or Sn atoms, signifying robust hydrogen-dominated bonding. A second prominent valence feature, situated nearer to the Fermi level at around -3 to -2 eV, is distinguished by a wider TDOS peak due to significant hybridization between metal p states and H-1s orbitals, hence affirming the existence of metal–hydrogen bonding states. As the VBM is approached, the density of states progressively diminishes to zero. The PDOS study indicates that the valence band edge is mostly influenced by hybridized H-1s and Ge (Sn)-p orbitals. The TDOS in the conduction band region displays a progressive increase above the band gap, accompanied by small intensity peaks predominantly derived from antibonding metal s and p states combined with H-1s orbitals. The strong spatial overlap and hybridization between the metal s/p and H-1s states lead to highly dispersive electronic bands near the conduction band minimum. This pronounced band curvature corresponds to a small electron effective mass (m^*). Since carrier mobility is inversely proportional to the effective mass ($\mu \propto 1/m^*$), this electronic structure supports efficient charge transport and enhanced carrier mobility, making these hydrides promising candidates for solar energy harvesting

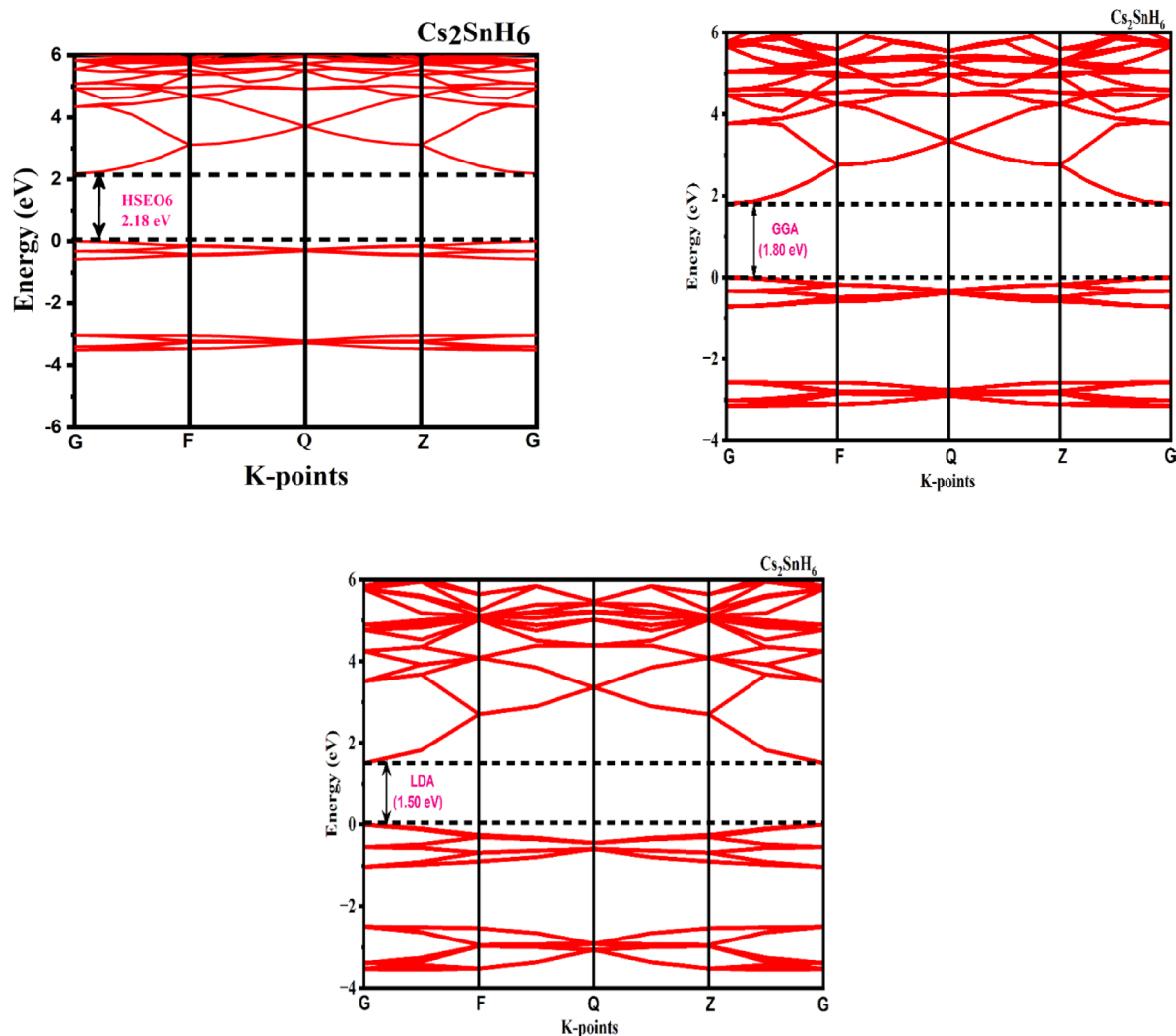


Fig. 5 (continued)

applications. Charge transport behavior was analyzed based on the curvature of the electronic band structure near the Γ -point. The conduction band minimum shows a highly dispersive nature, indicating light electron effective masses, while the valence band maximum is relatively flatter due to localized H-1s orbital contributions, suggesting heavier hole effective masses. This asymmetry in band dispersion implies favorable charge separation and reduced recombination probability, which is beneficial for optoelectronic applications. At elevated energies, generally ranging from +4 to +8 eV, the influence of d orbitals becomes more significant, indicating a stronger metal-centered nature in the upper conduction band. Cs-derived states remain insignificant near the band margins and are only detectable at much elevated energies. Likewise, in PDOS-like band structures, variations occur due to the use of GGA and LDA exchange–correlation functionals. The comparison indicates that the TDOS in GGA shifts to elevated energies relative to LDA, leading to an expanded band gap and less overlap between valence and conduction states, while maintaining the overall shape and orbital characteristics of the DOS. This phenomenon arises because the LDA overestimates electron correlation, leading to underestimated band gaps and compressed energy levels⁶¹. A comparison of the two materials within the same functional context reveals that Cs_2SnH_6 exhibits higher conduction band onset and more significant metal-related contributions in the conduction region than Cs_2GeH_6 , which aligns with its larger band gap. TDOS and PDOS show that hydrogen-rich bonding states dominate the valence band, while metal–hydrogen antibonding interactions define the conduction

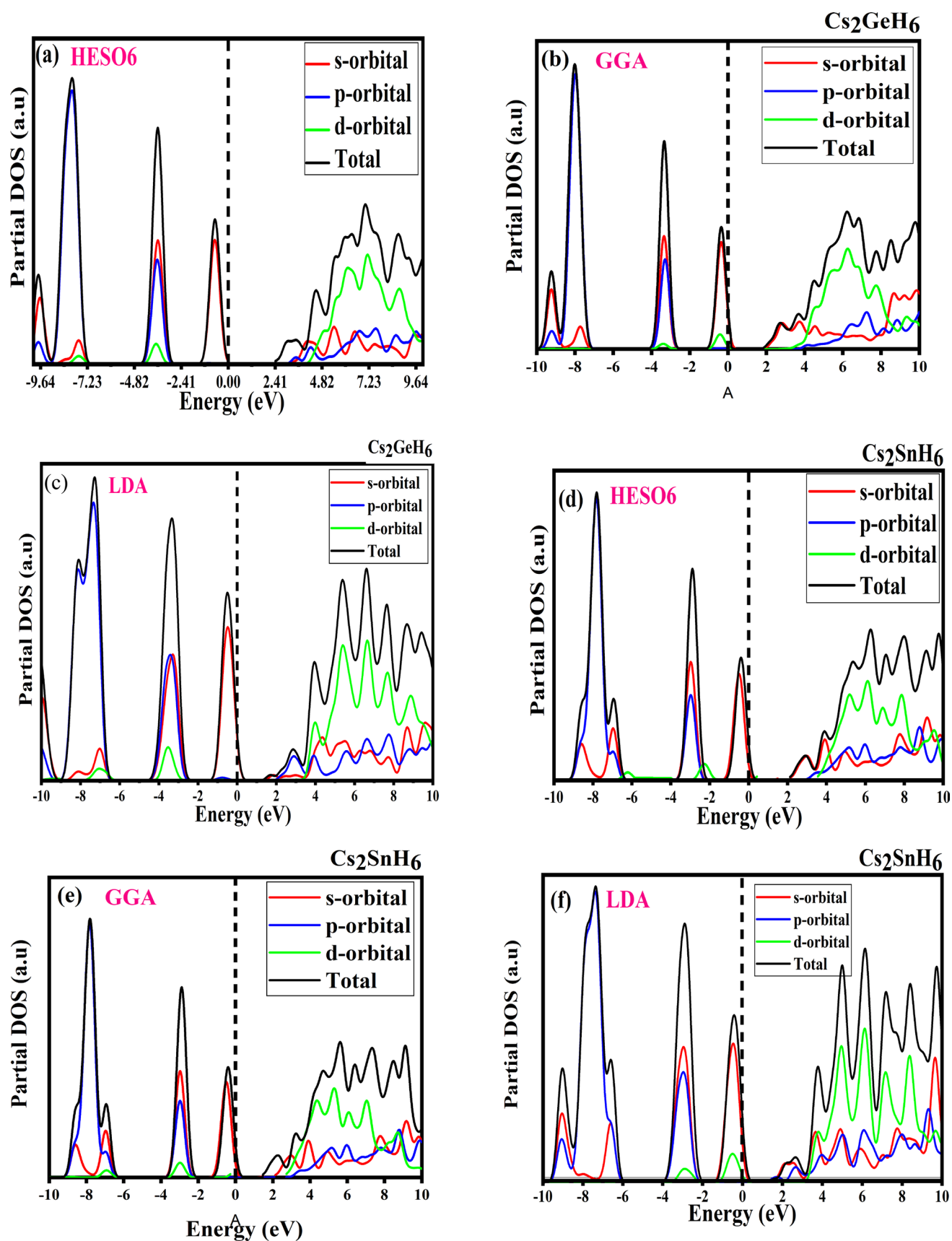


Fig. 6 Total and partial density of state (PDOS) of Cs_2GeH_6 and Cs_2SnH_6 with HESO6, GGA and LDA respectively.

band. Systematic variations in these electronic states account for the observed functional and material-dependent differences in the electronic band gap. Beyond the ideal band-edge electronic structure, intrinsic point defects play an important role in the optoelectronic performance of perovskite materials. In Cs_2GeH_6 and Cs_2SnH_6 , the zero-dimensional (0D) vacancy-ordered structure is expected to enhance defect tolerance compared to conventional ABX_3 perovskites. In these isolated $[\text{MH}_6]^{2-}$ units, native defects such as Cs or H vacancies are unlikely to introduce deep mid-gap states. Instead, defect-induced states are expected to remain shallow and near the band edges due to strong orbital hybridization. As a result, the fundamental band gap is largely preserved, supporting long carrier lifetimes and stable optoelectronic performance.

The distinct separation between hydrogen-dominated valence bands and metal–hydrogen antibonding conduction bands, together with the large band gaps, indicates that Cs_2GeH_6 and Cs_2SnH_6 are electronically stable wide-band-gap semiconductors. These characteristics render them promising candidates for optoelectronic and energy-related applications, such as ultraviolet photodetectors, insulating layers, and hydrogen-rich materials in which strong metal–hydrogen bonding and electronic stability are essential.

Charge density analysis

Mulliken population analysis plays an important role in understanding the nature of chemical bonding in crystalline materials by revealing how electronic charge is distributed among constituent atoms. This method provides valuable quantitative information on atomic (partial) charges, bond populations, and bonding interactions, which helps distinguish between ionic and covalent contributions within a solid⁶². By analyzing the overlap of atomic orbitals, Mulliken population analysis allows the effective charge on each atom (α) to be determined (Eq. 10), offering insight into charge transfer mechanisms and the strength of interatomic bonding. Such information is essential for interpreting the electronic structure and bonding behavior of materials at the atomic level.

$$Q(\alpha) = \sum_k W_k \sum_{\substack{On \\ On}}^a \sum_{\substack{On \\ v}}^{\beta} 2P_{uv}(k) S_{uv}(k) \quad (10)$$

A positive Mulliken charge corresponds to electron loss and donor behavior, while a negative Mulliken charge indicates electron gain and acceptor behavior, with the magnitude reflecting the relative ionic or covalent contribution to bonding^{63,64}. In this study, Mulliken population analysis indicates a significant redistribution of electrical charge within the crystal lattice. A substantial transfer of electron density occurs from Cs atoms to the surrounding framework. Cs exhibits a positive charge of +1.27 e, indicating a predominantly ionic character in the structure. In contrast, hydrogen atoms accumulate electron density, resulting in a charge of −0.38 e. While the Mulliken analysis assigns a small negative charge to the Sn atoms (−0.24 e), this negative value is a well-known mathematical artifact arising from the spatial partitioning of the localized atomic basis set projections in heavy-element hydrides. To resolve this and verify the true physical electrostatic landscape, a topological Bader charge analysis was conducted. The grid-based Bader method yields a physically correct positive charge of +1.54 e for Sn (along with +0.85 e for Cs and −0.40 e for H), confirming its role as an electropositive electron donor. The Sn–H bond population value of 0.73 and an average bond length of 1.89 Å further support the presence of strong covalent bonding between Sn and hydrogen. The negative bond population (−0.08) and the hydrogen–hydrogen distance of approximately 2.68 Å indicate that the interaction between hydrogen atoms remains weak. The coexistence of strong ionic Cs–H interactions and covalent Sn–H bonds demonstrates that the hydride perovskite exhibits mixed bonding characteristics. The strong ionic character of Cs–H interactions provide long-range electrostatic stabilization by anchoring the $[\text{MH}_6]^{2-}$ octahedra and suppressing structural distortions, thereby enhancing overall lattice stability. This mixed bonding also influences the material's anisotropic electrical properties.

Constant bond lengths and uniformly distributed charges among symmetry-equivalent atomic positions indicate a high degree of electronic homogeneity within the crystal, which is closely associated with dynamical stability⁶⁵. The structural and electronic characteristics obtained in this study are in strong agreement with

previously reported results for similar hydride perovskites, such as Cs_2GeH_6 and Cs_2SnH_6 , thereby supporting the reliability of the present computational methodology. Compared with Mulliken population analysis, the Bader charge analysis provides a more reliable description of charge transfer because it is based on the topology of the electron density rather than basis-set-dependent atomic populations. The observed charge transfer and mixed ionic–covalent bonding provide a solid basis for understanding the electronic structure and the optical properties discussed in the following sections. The electron transfer from Cs and the metal atoms to hydrogen influences the distribution of electronic states, which contributes to the calculated band gaps and the strong optical absorption of both compounds.

Electron density difference and bonding analysis

The electron density difference maps depicted in Fig. 7 offer supplementary data about the bonding characteristics in Cs_2GeH_6 and Cs_2SnH_6 . The maps demonstrate a significant concentration of electron density near the hydrogen atoms, along with a reduction at the Ge and Sn centers, signifying electron transfer from the metal atoms to hydrogen. This behavior aligns with the charge distribution patterns derived by Mulliken population analysis. The diminished electron density around the Cs atoms confirms their function as electron donors in the lattice. The redistribution of charge along the Ge–H and Sn–H bonds indicate significant covalent interactions with ionic contributions. A more pronounced localization of electron density around hydrogen is noted in Cs_2GeH_6 relative to Cs_2SnH_6 , attributable to the greater electronegativity of Ge and, subsequently, enhanced Ge–H bonding. The consistency between electron density difference maps and Mulliken charge analysis underscores the hybrid ionic–covalent bonding nature of these hydride perovskites.

Optical properties

The analysis of optical properties provides critical insights into the interactions between electromagnetic radiation and materials. In this study, key optical characteristics, such as optical conductivity, reflectivity, refractive index $n(\omega)$, energy loss function $L(\omega)$, and dielectric response were determined. These optical quantities were derived from the complex frequency-dependent dielectric function, $\epsilon(\omega)$, expressed as⁶⁵

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

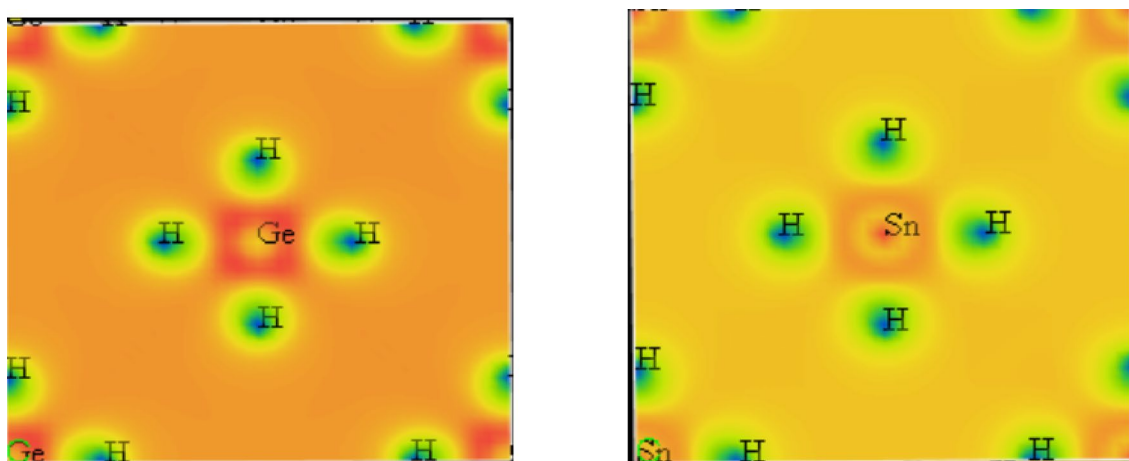


Fig. 7 Electron density difference maps of Cs_2GeH_6 and Cs_2SnH_6 . Blue/red regions indicate electron density accumulation around hydrogen atoms, while depletion occurs at Ge/Sn and Cs centers, highlighting ionic Cs–H interactions and covalent M–H bonding.

The real part, $\epsilon_1(\omega)$, and the imaginary part, $\epsilon_2(\omega)$, describe the dispersive and absorptive properties of the material, respectively, and were evaluated using established formulas reported in the literature. To maintain absolute internal consistency with electronic structures, the optical properties were systematically evaluated using the high-level HSE06 hybrid functional alongside the standard GGA-PBE and LDA approximations⁶⁷.

The real component of the dielectric function, $\epsilon_1(\omega)$, characterizes the dispersive properties of the material and quantifies its ability to polarize and store electric energy under an external electromagnetic field. Figure 8a,c display the energy-dependent $\epsilon_1(\omega)$ for Cs_2GeH_6 and Cs_2SnH_6 . For both materials, ϵ_1 exhibits high values in the low-energy region and gradually decreases with increasing photon energy, reflecting the typical behavior of wide-band-gap semiconductors. Under the HSE06 hybrid functional framework, the corrected, wider electronic band gaps result in a predictable, slight decrease in the static electronic polarizability compared to the semi-local GGA and LDA calculations. A pronounced minimum occurs near 9–10 eV, after which ϵ_1 slightly increases at higher energies. In the low-energy interval, Cs_2SnH_6 consistently shows a stronger dielectric screening response than Cs_2GeH_6 under HSE06, matching its lower hybrid band gap (2.18 eV vs. 2.41 eV), indicating stronger dielectric screening and greater electronic polarizability. This enhanced response results from the higher atomic density of Sn and the associated redistribution of electronic charge, which facilitates increased polarization under optical excitation. At higher photon energies (above 9 eV), the ϵ_1 curves for both compounds converge, suggesting that the dielectric response in this regime is less influenced by the choice of B-site cation, as electronic transitions occur far from the valence-band region.

The imaginary component of the dielectric function, $\epsilon_2(\omega)$, which reflects optical absorption resulting from interband electronic transitions, is shown in Fig. 8b,d. Both compounds show a clear absorption onset that is directly related to their fundamental band gaps. When the HSE06 hybrid functional is used instead of the conventional GGA/LDA approach, the absorption onset of $\epsilon_2(\omega)$ shifts to higher photon energies (blue shift). This change improves the prediction of the absorption edge by correcting the underestimation of the band gap obtained with GGA/LDA. According to the HSE06 results, Cs_2SnH_6 begins to absorb light at a lower photon energy than Cs_2GeH_6 , which is consistent with their direct electronic transitions at the Γ point. After the absorption edge, several strong peaks appear due to electronic transitions from the valence band to the conduction band. In the low-energy region (about 4–6 eV), both compounds show high ϵ_2 peak values, indicating strong interaction between light and the materials. Near 9–10 eV, Cs_2GeH_6 shows a slightly higher ϵ_2 response, suggesting differences in conduction band dispersion between the two compounds. At photon energies above 15 eV, the ϵ_2 spectra for both materials converge, indicating that high-energy optical excitations are largely independent of compositional differences and are determined by deeper electronic states.

The dielectric response demonstrates that Cs_2SnH_6 possesses superior optical and dielectric properties in the low- to mid-energy range compared to Cs_2GeH_6 , while both materials display similar behavior at higher energies. The enhanced dielectric strength and absorption observed in the Sn-based hydride are attributed to its greater electronic polarizability and modified band structure, highlighting its potential for applications in visible-light-driven photovoltaic and optoelectronic technologies.

Figure 9a–d depict the frequency-dependent refractive index, $n(\omega)$, and extinction coefficient, $k(\omega)$, of Cs_2GeH_6 and Cs_2SnH_6 , providing comprehensive insight into their optical characteristics. The refractive index is a fundamental parameter for evaluating the applicability of materials in optoelectronic devices, as higher $n(\omega)$ values strengthen light–matter interaction, enhance optical confinement, and can improve overall device efficiency⁶⁸. An ideal operating spectral window is typically characterized by a large refractive index accompanied by a low extinction coefficient, ensuring strong light propagation with minimal optical losses. In the low-energy region, both compounds exhibit relatively high $n(\omega)$ values, with Cs_2SnH_6 consistently showing a stronger response than Cs_2GeH_6 , particularly around 4–5 eV, indicating enhanced electronic polarizability. As the photon energy increases, $n(\omega)$ decreases gradually for both systems, displaying normal dispersion behavior, followed by a pronounced minimum near 9–10 eV and a slight recovery at higher energies. These similar trends observed along different polarization directions confirm the nearly isotropic optical nature of the cubic structures. The extinction coefficient, which represents the attenuation of light within the material, remains negligible at very low photon

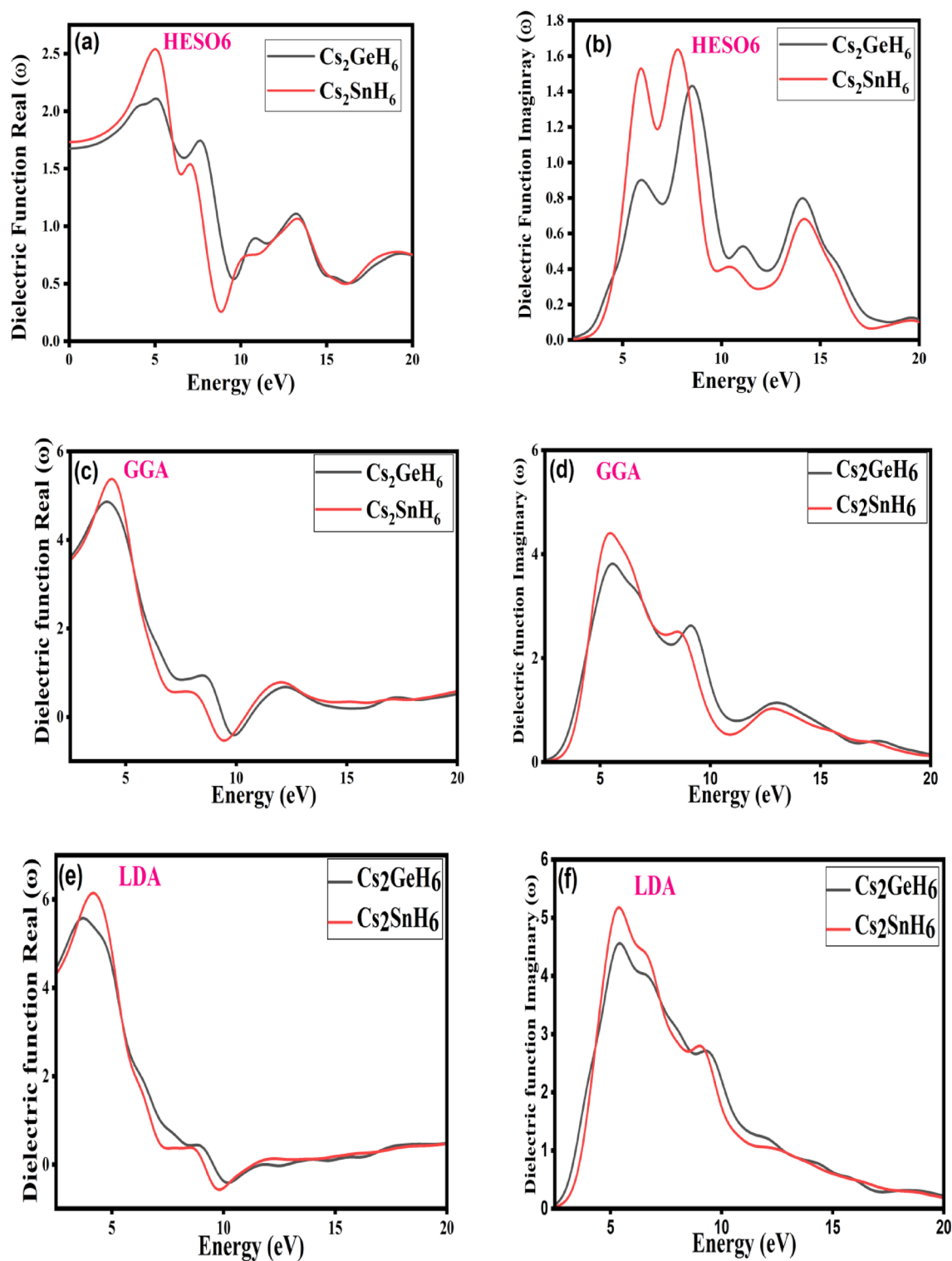


Fig. 8 Dielectric functions of Cs_2GeH_6 and Cs_2SnH_6 . (a,b) Real (ϵ_1) and imaginary (ϵ_2) parts calculated using HESO6; (c,d) Real and imaginary parts calculated using GGA and (e,f) Real (ϵ_1) and imaginary (ϵ_2) parts calculated using LDA

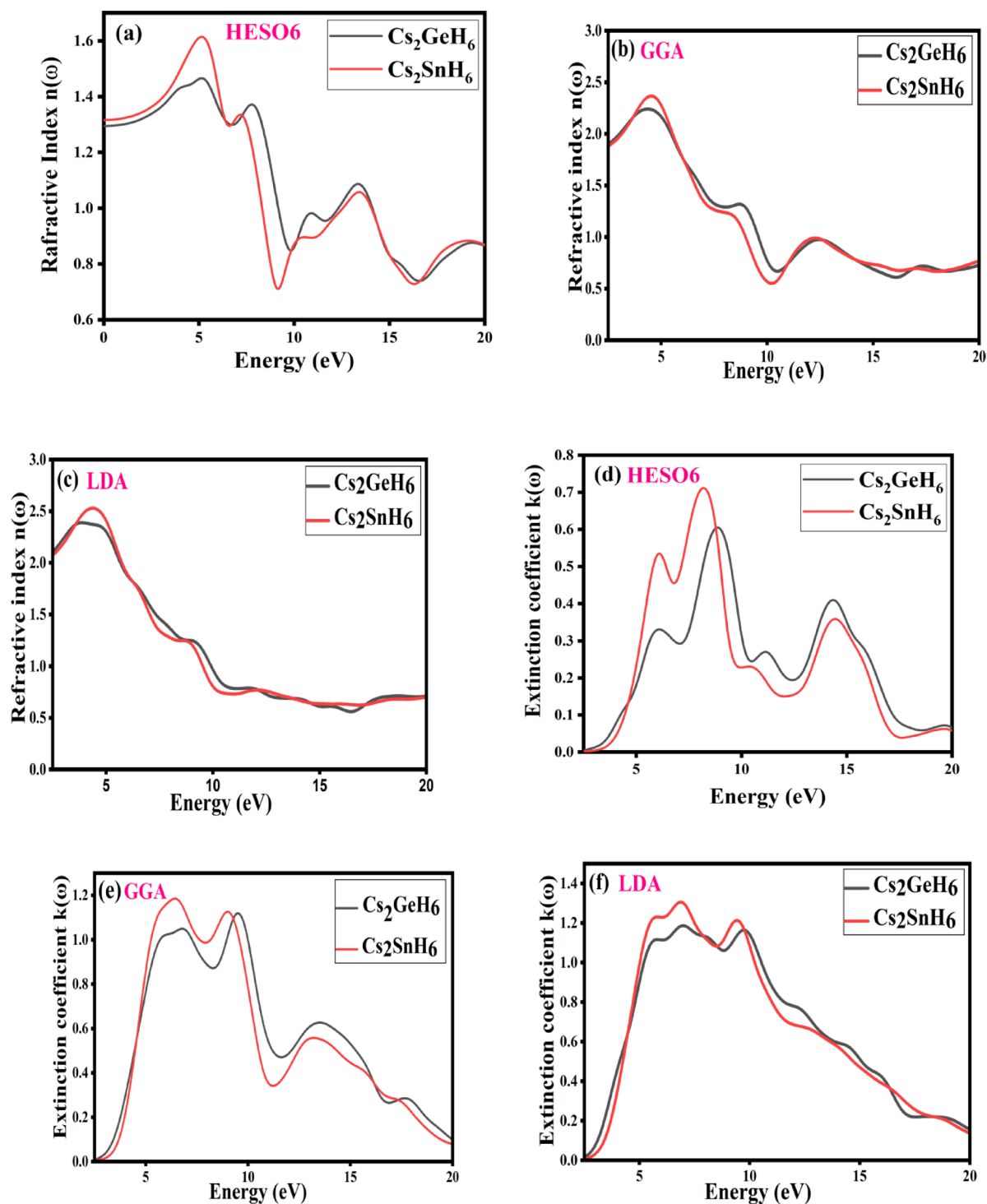


Fig. 9 Frequency-dependent refractive index $n(\omega)$ and extinction coefficient $k(\omega)$ of Cs_2GeH_6 and Cs_2SnH_6 using HESO6 (a,b), GGA (c,d) and LDA (e,f)

energies, signifying optical transparency below the absorption edge, and increases sharply across the visible-to-near-UV region, reflecting the onset of interband electronic transitions. Under the HSE06 hybrid functional framework, the onset of $k(\omega)$ exhibits a distinct blue shift relative to standard LDA/GGA predictions, aligning perfectly with the corrected fundamental electronic band gaps. The spectral profile of $k(\omega)$ closely follows that of the

imaginary part of the dielectric function, $\epsilon_2(\omega)$, confirming that optical absorption is governed by the same electronic transitions responsible for dielectric losses. In this region, Cs_2SnH_6 exhibits higher $k(\omega)$ values, indicating stronger absorption and enhanced light–matter coupling, whereas Cs_2GeH_6 shows comparatively weaker attenuation. Since both the refractive index and extinction coefficient are directly derived from the real and imaginary components of the dielectric function, $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$, their behavior reflects the underlying electronic structure of the materials. Additionally, the frequency-dependent optical conductivity, expressed as $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$, further complements this analysis by describing the dissipative and reactive response of charge carriers under optical excitation. Overall, the combined refractive index, extinction coefficient, dielectric, and conductivity results demonstrate that Cs_2SnH_6 offers a stronger low-energy optical response, while both compounds maintain stable and predictable behavior at higher photon energies, highlighting their suitability for broad-spectrum visible-light harvesting, thin-film photovoltaics, and dielectric-related optoelectronic applications.

Figure 10 presents a detailed analysis of the optical response of Cs_2GeH_6 and Cs_2SnH_6 , including calculated optical conductivity, absorption coefficient, reflectivity, and energy loss function as functions of incident photon energy, using the LDA, GGA-PBE, and HSE06 hybrid exchange–correlation functionals. Figure 10a,b show that the optical conductivity $\sigma(\omega)$ remains nearly zero at low photon energies, confirming the absence of free-carrier contributions and the wide-band-gap semiconducting nature of both materials. A sharp increase in $\sigma(\omega)$ marks the onset of interband electronic transitions and directly corresponds to the optical band gap. Under the GGA approximation, the main conductivity peak appears between 5.5 and 7.0 eV, reaching a maximum of about 3.0 fs^{-1} . In contrast, the LDA results consistently exhibit a red shift, with the primary peak at lower energies (5.0 to 6.0 eV) and slightly higher intensities (approximately 3.4 fs^{-1}). The red shift observed in the LDA results is mainly due to its tendency to underestimate the electronic band gap. In contrast, the HSE06 hybrid functional provides a more accurate band gap, causing the optical conductivity onset to shift toward higher photon energies (blue shift). The optical conductivity starts near the calculated band gaps of 2.41 eV for Cs_2GeH_6 and 2.18 eV for Cs_2SnH_6 , indicating the minimum energy required for electronic transitions from the valence band to the conduction band. In all computational approaches, replacing Ge with Sn increases the optical conductivity and shifts spectral features to lower energies, indicating a higher probability of electronic transitions in Cs_2SnH_6 due to its reduced band gap.

The optical absorption coefficient, $\alpha(\omega)$, shown in Fig. 10c,d, further supports these results. Both compounds show very low absorption below the fundamental absorption edge. Once the photon energy reaches the band gap, the absorption coefficient increases rapidly across the visible to near-ultraviolet (UV) region due to the onset of interband electronic transitions. Compared with the GGA and LDA results, the HSE06 hybrid functional shifts the absorption edge toward higher photon energies (blue shift), which is consistent with the more accurate band gap values predicted by HSE06. LDA calculations consistently produce a red shift in the absorption spectra relative to GGA due to band gap underestimation. Crucially, under the accurate HSE06 description, Cs_2SnH_6 displays its absorption onset at a lower photon energy (2.18 eV) than Cs_2GeH_6 (2.41 eV). This confirms that the Sn-based material possesses a narrower fundamental gap under the hybrid functional framework and initiates visible-light harvesting earlier. In the GGA results, the main absorption peak for Cs_2GeH_6 reaches approximately $1.75 \times 10^5 \text{ a.u.}$ near 9.8 eV, with a secondary peak around 14 eV. In the LDA results, the primary peak shifts to about 9.5 eV with a slightly higher intensity of nearly $1.85 \times 10^5 \text{ a.u.}$ Although the absolute peak positions and intensities vary with the functional, the relative ordering remains unchanged, with the hybrid functional confirming the enhanced capacity of the Sn-based material for low-energy, visible-light absorption.

Figure 10e,f display the reflectivity spectra $R(\omega)$ for both materials. The reflectance remains moderate across the studied energy range, consistent with semiconducting behavior. A systematic red shift is again observed in the LDA data compared to GGA. Cs_2SnH_6 exhibits higher reflectivity than Cs_2GeH_6 throughout the main reflective region (5 to 12 eV), with a pronounced maximum near 10 eV reaching about 0.29 in the GGA calculation. This increased reflectivity in the Sn-based compound results from its higher refractive index, which is directly linked to its smaller band gap and enhanced dielectric response.

The energy loss function $L(\omega)$, depicted in Fig. 10g,h, characterizes collective electron excitations and plasmonic effects. Distinct peaks in $L(\omega)$ represent plasmon resonance energies, which shift to lower energies in the

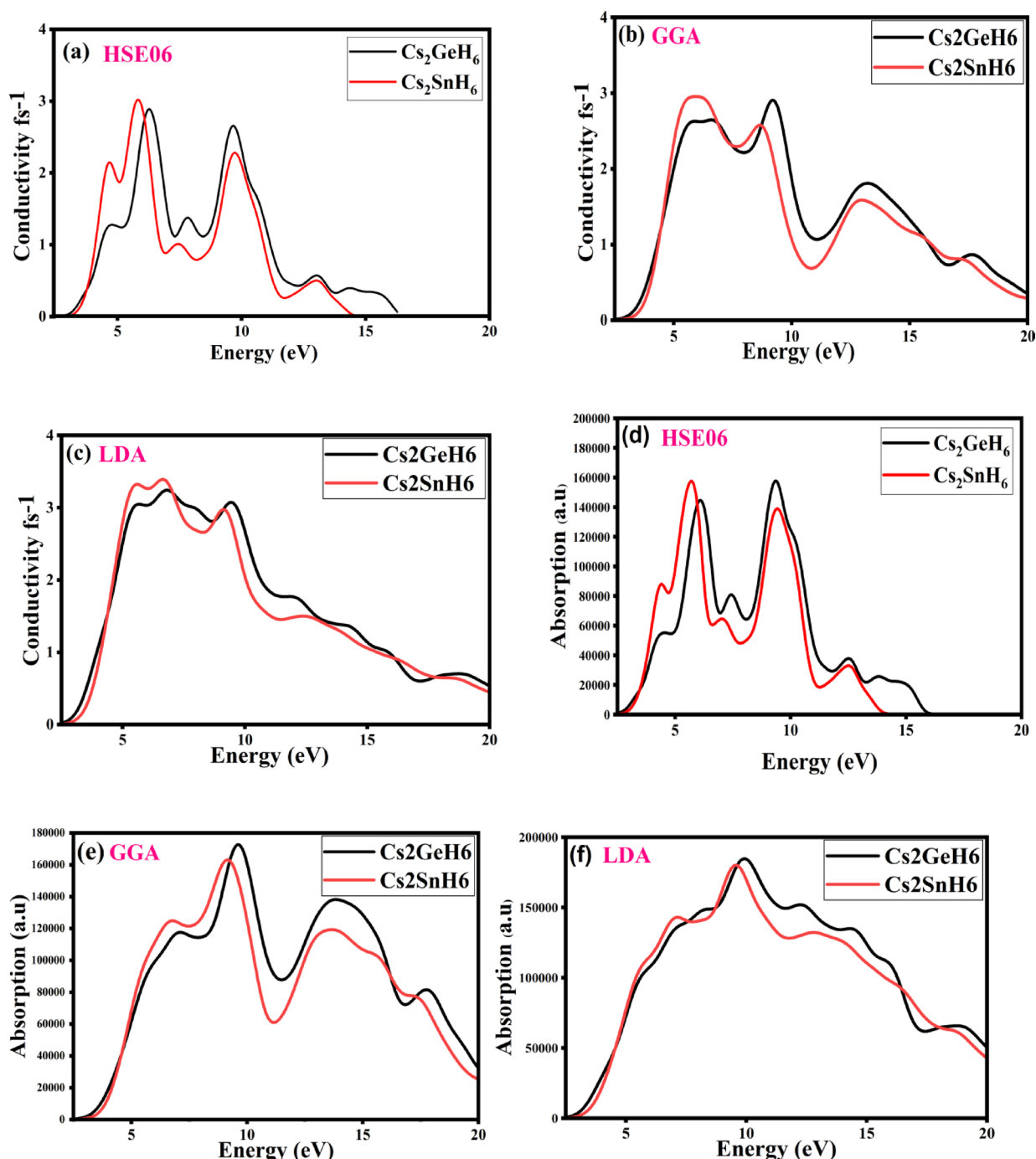


Fig. 10 Optical properties of Cs_2GeH_6 and Cs_2SnH_6 : optical conductivity $\sigma(\omega)$ (a–c), absorption coefficient $\alpha(\omega)$ (d–f), reflectivity $R(\omega)$ (g–i), and energy loss function $L(\omega)$ (j–l) calculated using HSE06, GGA and LDA.

LDA calculations compared to GGA due to the underestimation of the band gap. In contrast, the HSE06 hybrid functional shifts these energy-loss peaks toward higher photon energies (blue shift). This shift results from the more accurate description of the electronic structure provided by HSE06 and indicates a higher energy threshold for collective electronic excitations. Cs_2SnH_6 displays its main plasmon peak at a lower energy, around 11 eV, indicating that replacing Ge with the heavier Sn cation softens the plasmonic response and alters the high-frequency dielectric properties. a trend that remains fully consistent across all functional approximations including

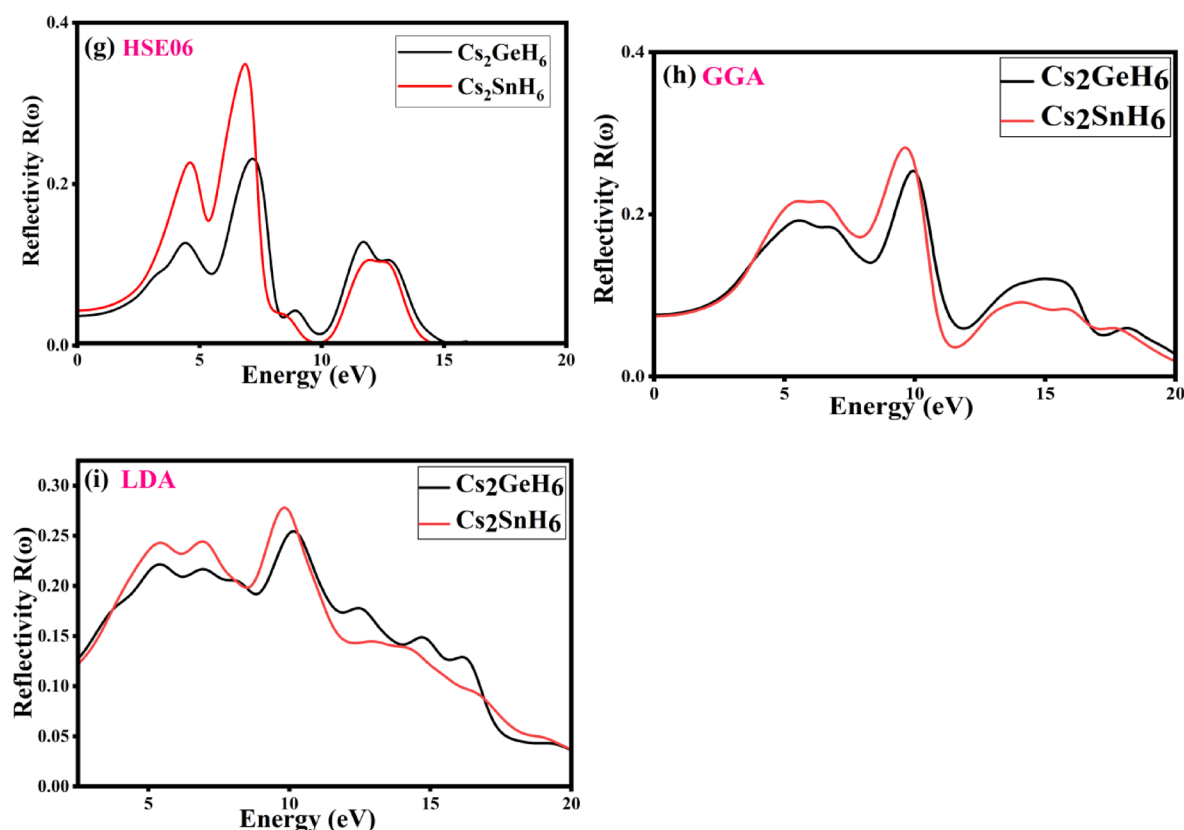


Fig. 10 (continued)

the high-level HSE06 hybrid method. In contrast, Cs_2GeH_6 exhibits a higher maximum loss intensity, reaching about 2.0 near 16.5 eV in the GGA calculation, which suggests stronger collective electron oscillations at higher photon energies.

In summary, the combined analysis of optical conductivity, absorption, reflectivity, and energy loss spectra reveals two clear trends. First, the choice of exchange–correlation functional primarily shifts the absolute thresholds of spectral features; while semi-local LDA calculations yield red shifts relative to GGA, the highly accurate HSE06 hybrid functional framework systematically blue-shifts the absorption edges and optical features, perfectly correcting the electronic band gap underestimations. Second, substituting Ge with Sn significantly enhances the low-energy optical response, resulting in higher conductivity, greater absorption, increased reflectivity, and lower plasmon energies. These results indicate that the heavier Sn cation reduces the optical band gap and increases electronic polarizability, thereby strengthening light–matter interactions at lower photon energies. In contrast, Cs_2GeH_6 shows a stronger optical response at higher photon energies. The HSE06 results also confirm that, although the optical spectra shift to higher energies compared with the GGA and LDA results, both materials maintain strong visible-light absorption. These findings suggest that Cs_2GeH_6 and Cs_2SnH_6 are promising materials for photovoltaic and optoelectronic applications.

To place Cs_2GeH_6 and Cs_2SnH_6 in context, we compare them with well-known perovskite systems. Lead-halide perovskites such as CsPbI_3 show excellent optoelectronic properties but suffer from toxicity and structural instability^{69,70}. In contrast, complex metal hydrides such as Ba_2MgH_6 usually have wide band gaps (>3.5 eV), which limits their use in optoelectronic devices and makes them more suitable for hydrogen storage applications⁷¹.

The present vacancy-ordered double perovskite hydrides overcome these limitations by balancing stability, toxicity-free composition, and suitable electronic properties. Standard GGA functionals underestimate the band gap⁷², while HSE06 gives improved values of 2.41 eV for Cs_2GeH_6 and 2.18 eV for Cs_2SnH_6 . These values fall in a

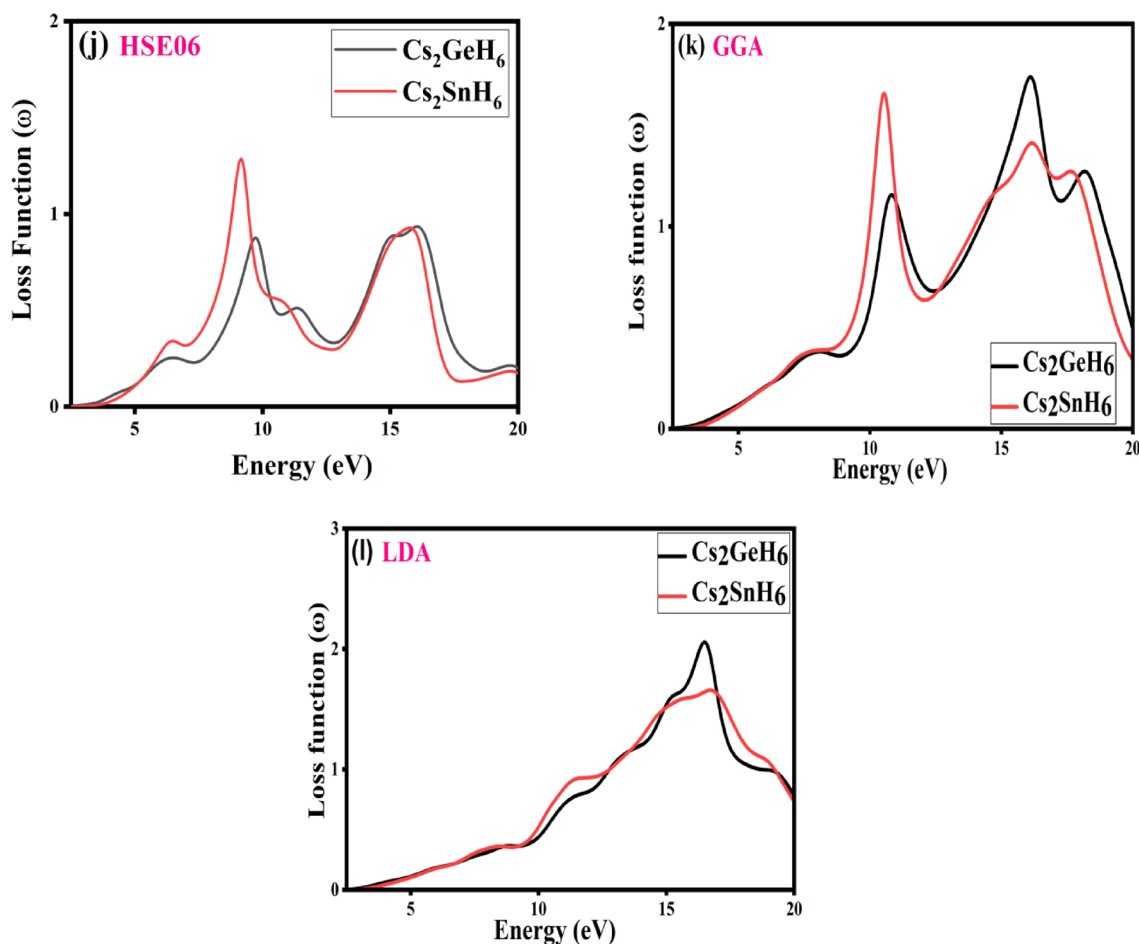


Fig. 10 (continued)

useful range for visible-light absorption. In addition, their relatively low Young's moduli indicate better mechanical flexibility compared to rigid halide perovskites, which is useful for flexible device applications⁷³.

Thermodynamic properties and lattice dynamics

Thermodynamic and lattice-dynamical properties are fundamental to assessing the stability, reliability, and practical applicability of functional materials under realistic operating conditions. In particular, temperature-dependent thermodynamic quantities offer valuable insight into lattice stability, vibrational behavior, and long-term performance, all of which are critical factors for optoelectronic and energy-related device applications^{74,75}. In this work, the thermodynamic behavior of the lead-free double perovskite hydrides Cs_2GeH_6 and Cs_2SnH_6 is investigated using phonon-derived quantities, including the phonon density of states (DOS), Debye temperature (θ^D), constant-volume heat capacity (C_v), entropy (S), enthalpy (H), and Gibbs free energy (G).

The phonon density of states, as shown in Fig. 2e, provides clear evidence of the dynamical stability of both compounds. The complete absence of imaginary phonon frequencies indicates that the optimized crystal structures correspond to true minima on the potential energy surface⁷⁶. The low-frequency region of the phonon spectrum is dominated by acoustic modes arising from vibrations of the heavier Cs and Ge/Sn atoms, which primarily govern the elastic and mechanical response of the lattice. In contrast, the high-frequency optical modes originate from localized vibrations of the light hydrogen atoms within the MH_6 octahedra, consistent with the large mass difference between constituent elements. A noticeable phonon softening is observed when transitioning from

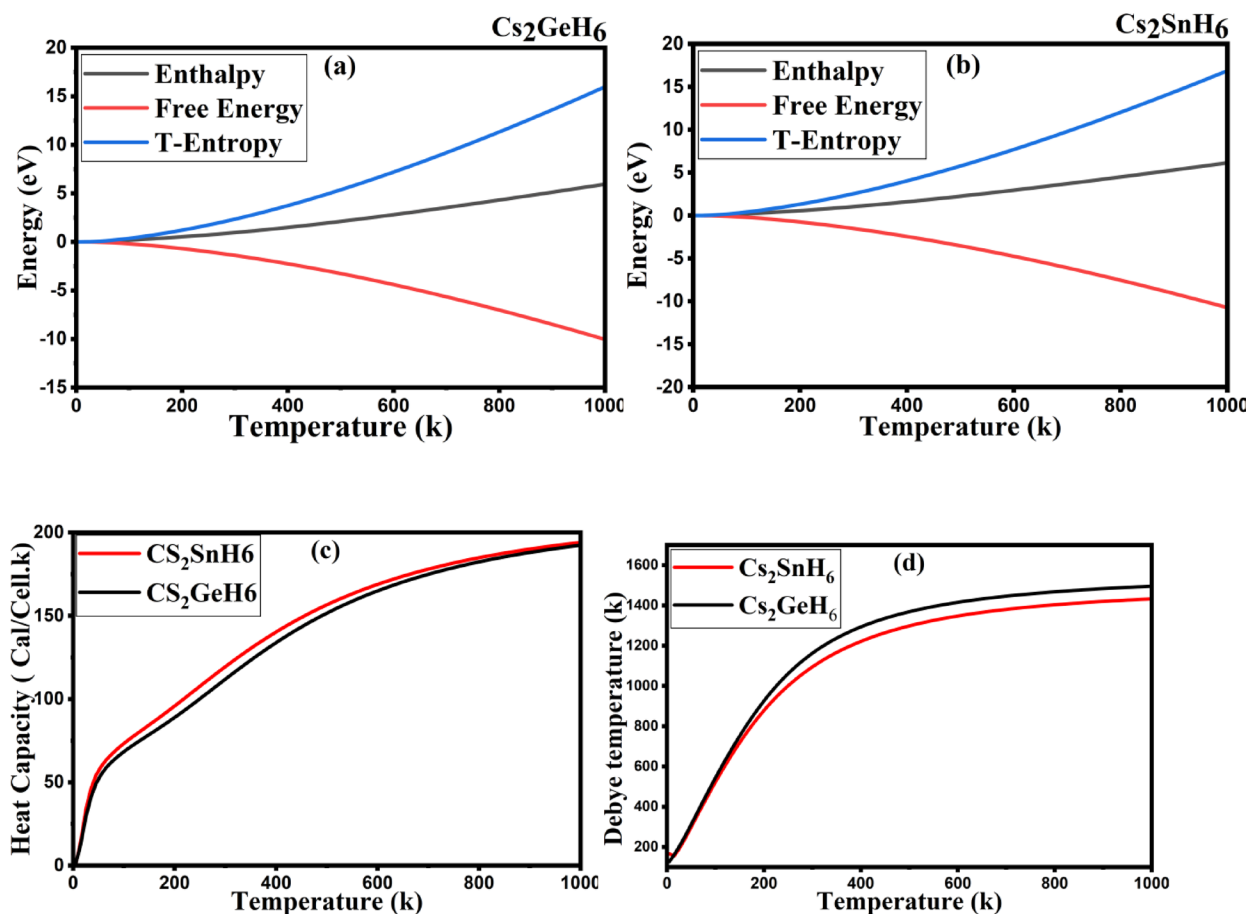


Fig. 11 Thermodynamic and lattice-dynamical properties of Cs_2GeH_6 and Cs_2SnH_6 : (a,b) temperature dependence of enthalpy, Gibbs free energy, and entropy, (c) constant-volume heat capacity $C_v(T)$, (d) Debye temperature $\theta_D(T)$, and

Cs_2GeH_6 to Cs_2SnH_6 , manifested as a redshift of vibrational modes in the phonon spectrum. This behavior is attributed to the larger atomic mass of Sn relative to Ge and reflects enhanced lattice flexibility in the Sn-based hydride. Such lattice softening can influence electron–phonon interactions, which are known to affect charge-carrier transport and optoelectronic performance^{77,78}.

The lattice rigidity and overall bonding strength are characterized by the Debye temperature (θ_D), as shown in Fig. 11d. The Debye temperature is a fundamental thermodynamic parameter describing lattice vibrations, including the temperature dependence of specific heat and intrinsic thermal stability⁷⁹. For both compounds, θ_D increases with temperature due to the activation of higher-energy vibrational modes. Notably, Cs_2GeH_6 exhibits a higher Debye temperature than Cs_2SnH_6 , indicating stronger bonding and a stiffer lattice framework in the Ge-based hydride. From a thermal transport perspective, the lattice thermal conductivity is proportional to the cube of the Debye temperature ($\kappa_L \propto \theta_D^3$) according to Slack’s formulation, indicating higher heat dissipation capability for Cs_2GeH_6 . Since room temperature (300 K) is below θ_D , lattice dynamics are dominated by low-frequency acoustic phonons, where Umklapp scattering is reduced, leading to longer phonon mean free paths and efficient thermal transport. Materials with higher Debye temperatures generally show greater resistance to thermal deformation, which is beneficial for optoelectronic devices under thermal cycling conditions⁷⁹.

The thermal energy storage behavior is described by the constant-volume heat capacity (C_v), shown in Fig. 11c, which arises primarily from lattice vibrations. At low temperatures, C_v follows the characteristic Debye T^3 law, reflecting the dominance of acoustic phonon modes. With increasing temperature, C_v gradually approaches the

classical Dulong–Petit limit ($3nR$), corresponding to the saturation of vibrational degrees of freedom and the reduced validity of the harmonic approximation⁸¹ The phonon-based heat capacity can be expressed as^{82–85}:

$$C_V(T) = k_B \int_0^{\infty} \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} g(\omega) d\omega \quad (12)$$

where $g(\omega)$ is the phonon density of states. This behavior highlights the ability of both hydrides to efficiently absorb and dissipate thermal energy, an important factor for maintaining device stability and performance.

Entropy (S), which arises from thermally induced atomic disorder, increases monotonically with temperature for both compounds, reflecting enhanced vibrational activity within the lattice⁸⁶. The phonon-derived entropy can be written as⁸⁷:

$$S(T) = k_B \int_0^{\infty} \left[\frac{\hbar\omega/k_B T}{e^{\hbar\omega/k_B T} - 1} - \ln(1 - e^{-\hbar\omega/k_B T}) \right] g(\omega) d\omega \quad (13)$$

The enthalpy (H) also increases steadily with temperature as thermal energy is absorbed by the lattice. The overall thermodynamic stability of the systems is ultimately determined by the Gibbs free energy, defined as:

$$G(T) = H(T) - TS(T) \quad (14)$$

As shown in Fig. 11a,b, the Enthalpy, Entropy, and Gibbs free energy are plotted as a function of temperature. The Gibbs free energy decreases monotonically with increasing temperature for both Cs_2GeH_6 and Cs_2SnH_6 , indicating thermodynamic favorability and spontaneous stability over the investigated temperature range. This continuous reduction in free energy confirms that both materials remain energetically stable at elevated temperatures, supporting their potential for long-term integration into hydrogen-based energy systems and optoelectronic architectures.

Conclusions

In this work, we performed systematic first-principles calculations to study the structural, electronic, optical, thermodynamic, and mechanical properties of the lead-free vacancy-ordered double perovskite hydrides Cs_2GeH_6 and Cs_2SnH_6 . Structural analysis confirmed that both compounds are thermodynamically, dynamically, and mechanically stable in the cubic $Fm\bar{3}m$ phase. This is supported by negative formation energies and the complete absence of imaginary phonon modes. Electronic structure calculations revealed that both hydrides are direct-band-gap semiconductors at the Γ -point, with PBE-calculated gaps of 1.60 eV (Cs_2GeH_6) and 1.80 eV (Cs_2SnH_6), making them suitable for visible-light optoelectronic applications. Furthermore, the HSE06 hybrid functional provides corrected fundamental band gap values of 2.41 eV for Cs_2GeH_6 and 2.18 eV for Cs_2SnH_6 , offering a more accurate and rigorous description of the electronic transitions. Bonding analysis, including Mulliken population and electron density difference maps, showed a mixed ionic–covalent character, dominated by strong metal–hydrogen interactions within the $[\text{MH}_6]^{2-}$ octahedra. Optical properties were analyzed through optical conductivity, absorption, reflectivity, and energy loss spectra. Two main trends were observed: (i) the choice of exchange–correlation functional mainly shifts the spectral positions, with LDA giving red shifts compared to GGA, while the high-level HSE06 functional systematically corrects these thresholds via a predictable blue shift that perfectly mirrors the updated electronic band gaps and (ii) substituting Ge with Sn enhances the low-energy optical response, leading to higher conductivity, stronger absorption, increased reflectivity, and lower plasmon energies. This makes Cs_2SnH_6 especially promising for optoelectronic devices. Mechanical properties, calculated from elastic constants and derived parameters (B , G , E , ν , H), indicate that Cs_2GeH_6 is stiffer, while Cs_2SnH_6 is

softer, which allows it to accommodate strain in thin-film devices. ELATE analysis shows that both compounds exhibit near-isotropic elastic behavior, ensuring uniform electronic and optical responses and structural resilience under mechanical and thermal stress. Thermodynamic modeling confirmed thermal stability up to 1000 K, with Cs_2GeH_6 showing higher lattice rigidity as seen from its Debye temperature. The monotonic decrease in Gibbs free energy across the temperature range further highlights energetic favorability and device applicability. Overall, Cs_2GeH_6 and Cs_2SnH_6 are structurally robust, thermally stable, and mechanically resilient, with tunable electronic and optical properties. The enhanced low-energy optical response of Cs_2SnH_6 , together with elastic and thermal stability, makes both hydrides promising candidates for next-generation lead-free perovskite-based photovoltaic and optoelectronic technologies. The present findings are based on first-principles calculations, and future experimental studies are needed to validate the predicted properties of these hydride perovskites.

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Author contributions Zeshan Ahmed: Conceptualization, Methodology, DFT Calculation, Formal analysis, Visualization, Writing—review & editing, Supervision. Salih Nawaz: Investigation, Data curation, Formal analysis, Writing—original draft. Abdullatif Hakami: Supervision, Validation, Formal analysis, Project Administration. Sanam Bashir: Review & editing. Funding acquisition, Resources Sunila Bakhs: Writing—review & editing. Mohamed Yusuf: Data curation, Writing—review & editing. Rageh K. Hussein: Conceptualization, Writing – review & editing.

Data availability The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Competing interests The authors declare no competing interests.

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