

RESEARCH ARTICLE

# Phase-Dependent Structural, Electronic, and Optical Properties of Lead-Free CsSnI<sub>3</sub>: A First-Principles DFT+U Study

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**ABSTRACT:** Cesium tin iodide (CsSnI<sub>3</sub>) is a promising lead-free perovskite for photovoltaic applications; however, its four polymorphs ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ) exhibit distinct structural, electronic, and optical properties. While the yellow  $\delta$ -phase is thermodynamically stable, its wide band gap limits photovoltaic performance, whereas the metastable black phases show narrower band gaps but lack systematic comparison within a unified computational framework. Here, density functional theory (DFT) calculations using CASTEP were performed to investigate all polymorphs. To overcome band-gap underestimation, a consistent DFT+U approach was employed. The Hubbard parameters were calibrated using the experimentally validated  $\gamma$ -phase, yielding  $U = 3.29$  eV for Sn-5s and  $U = 4.29$  eV for I-5p, then applied uniformly to all phases, enabling unbiased comparison. The calculated band gaps are 1.10 eV ( $\alpha$ ), 1.20 eV ( $\beta$ ), 1.30 eV ( $\gamma$ ), and 3.00 eV ( $\delta$ ). The  $\delta$ -phase is energetically most stable, whereas the  $\gamma$ -phase exhibits optimal optoelectronic performance, including a band gap consistent with experiment (1.27–1.30 eV), strong absorption ( $\alpha > 10^5$  cm<sup>-1</sup>), and enhanced dielectric screening. These results show that stability alone is insufficient and identify the  $\gamma$ -phase as the most promising candidate for CsSnI<sub>3</sub>-based photovoltaics.

**Keywords:** Lead-free perovskites; CsSnI<sub>3</sub> polymorphs; DFT; CASTEP; DFT+U; Photovoltaic solar cells

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## 1. INTRODUCTION

Metal halide perovskites have emerged as a versatile class of materials for optoelectronic applications owing to their

tunable crystal chemistry, flexible electronic structure, and strong light-matter interaction [1, 2]. These characteristics have enabled rapid advances in photovoltaics, light-emitting diodes, photodetectors, and radiation-sensing technologies. From a materials-design perspective, the exceptional performance of perovskites is closely linked to their soft lattice, corner-sharing octahedral framework, and highly hybridized electronic states near the band edges, which collectively give rise to strong optical absorption and favorable charge-transport characteristics [1, 3].

Despite their technological promise, conventional lead-based perovskites face significant challenges associated with environmental toxicity and long-term chemical stability [4-6]. Lead toxicity poses serious environmental and health concerns, motivating regulatory restrictions and driving the search for sustainable alternatives [5-7]. These limitations

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have stimulated extensive efforts to develop lead-free materials that retain the advantageous optoelectronic properties of lead halides while offering improved environmental compatibility. Among the proposed candidates, tin-based halide perovskites have attracted considerable attention due to the similar electronic configuration of Sn<sup>2+</sup> and Pb<sup>2+</sup> and their ability to form perovskite-related structures with relatively narrow band gaps [8–10].

Cesium tin iodide (CsSnI<sub>3</sub>) represents a prototypical lead-free perovskite system exhibiting pronounced polymorphism. It crystallizes in four distinct phases: cubic ( $\alpha$ ), tetragonal ( $\beta$ ), black orthorhombic ( $\gamma$ ), and yellow orthorhombic ( $\delta$ ) [11, 8]. These polymorphs differ substantially in symmetry, octahedral connectivity, lattice distortion, and thermodynamic stability, leading to marked variations in their electronic and optical characteristics. While the yellow  $\delta$  phase is generally identified as the thermodynamic ground state, its wide band gap limits its utility for visible-light applications. In contrast, the perovskite-derived  $\alpha$ ,  $\beta$ , and  $\gamma$  phases exhibit narrower band gaps and enhanced optoelectronic activity compared with the non-perovskite  $\delta$  phase, making them attractive for photovoltaic and related applications [8, 9, 12].

A critical challenge facing CsSnI<sub>3</sub>-based devices is the susceptibility of Sn<sup>2+</sup> to oxidation to Sn<sup>4+</sup>, which degrades device performance and limits ambient stability [13, 14]. Various strategies have been proposed to mitigate this issue, including the use of reducing atmospheres during fabrication, chemical additives such as SnF<sub>2</sub>, and compositional engineering through halide mixing [15, 16]. While the present computational study focuses on intrinsic properties of stoichiometric CsSnI<sub>3</sub> polymorphs, future investigations should address oxidation stability and defect chemistry.

A systematic understanding of how structural distortion, octahedral tilting, and bonding characteristics govern phase stability and intrinsic electronic properties in CsSnI<sub>3</sub> is therefore essential. First-principles density functional theory (DFT) provides a robust framework for addressing this challenge by enabling consistent evaluation of lattice parameters, relative phase stability, electronic structure, and optical response across competing polymorphs [1, 4]. Semi-local DFT approaches offer a computationally efficient and physically transparent description of structural trends, phase competition, orbital contributions, and qualitative electronic behavior, making them well suited for comparative investigations of polymorphic materials. However, previous computational studies often employ different exchange–correlation treatments or phase-dependent parameter fitting, which complicates direct comparison of phase-dependent properties and may introduce inconsistencies in reported trends.

In this work, DFT calculations are performed using CASTEP [17] to systematically investigate the structural stability, relative energetics, electronic structure, and optical response of all four CsSnI<sub>3</sub> polymorphs ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ) at the semi-local level. To ensure a consistent and physically meaningful comparison, a unified DFT+U framework is

adopted in which the Hubbard parameters are calibrated using experimentally validated data for the  $\gamma$  phase and subsequently applied uniformly across all polymorphs. This approach represents a key methodological advancement by eliminating parameter inconsistencies and enabling direct evaluation of intrinsic structure–property relationships.

## 2. COMPUTATIONAL METHODS

### 2.1. Density Functional Theory Framework

All first-principles calculations were carried out within the framework of density functional theory (DFT) using a plane-wave pseudopotential approach as implemented in the Cambridge Sequential Total Energy Package (CASTEP) [17, 18]. Exchange–correlation effects were treated within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional [19]. Electron–ion interactions were described using on-the-fly-generated ultrasoft pseudopotentials [20]. Scalar relativistic effects were implicitly included through the pseudopotential construction. Electronic occupations were treated using CASTEP’s fixed-occupancy scheme for non-metallic systems. The explicitly treated valence electron configurations were Cs (6s<sup>1</sup>), Sn (5s<sup>2</sup>5p<sup>2</sup>), and I (5s<sup>2</sup>5p<sup>2</sup>).

### 2.2. Numerical Convergence and Benchmark Strategy

Convergence tests were performed using the cubic  $\alpha$  phase of CsSnI<sub>3</sub> as a benchmark reference structure [8, 21]. Plane-wave cutoff energies in the range of 300–700 eV and Monkhorst–Pack k-point meshes of increasing density were tested [22]. A cutoff energy of 500 eV was found to yield well-converged structural and electronic properties. A 5×5×5 Monkhorst–Pack grid was employed for the cubic  $\alpha$  phase, while symmetry-adapted meshes of comparable density were used for the lower-symmetry  $\beta$ ,  $\gamma$ , and  $\delta$  phases. Electronic self-consistency was achieved using a total-energy convergence threshold of 10<sup>−6</sup> eV per atom.

### 2.3. Structural Optimization

Geometry optimizations were performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) quasi-Newton minimization algorithm [23]. Both lattice vectors and internal atomic coordinates were fully relaxed within the intrinsic crystallographic symmetry of each phase. Convergence was achieved when the change in total energy fell below 10<sup>−6</sup> eV per atom and residual atomic forces were reduced below standard plane-wave DFT thresholds. For the orthorhombic phases, the optimized lattice parameters are reported in the conventional crystallographic setting [8, 11].

### 2.4. Formation Energy and Relative Phase Stability

The thermodynamic stability of the CsSnI<sub>3</sub> polymorphs was evaluated using two complementary approaches: (i) calculation of formation energies with respect to elemental reference states, and (ii) comparison of relative total energies to establish phase ordering.

#### 2.4.1. Formation Energy Analysis

The formation energy ( $E^f$ ) quantifies the thermodynamic driving force for compound formation and is defined as:

$$E_{form} = E(\text{CsSnI}_3) - [E(\text{Cs}) + E(\text{Sn}) + \frac{3}{2}E(\text{I}_2)] \quad (1)$$

Where  $E(\text{CsSnI}_3)$  denotes the total energy per formula unit of the CsSnI<sub>3</sub> polymorph, while  $E(\text{Cs})$ ,  $E(\text{Sn})$ , and  $E(\text{I}_2)$  correspond to the total energies per atom of elemental cesium (bcc), tin ( $\beta$ -Sn), and solid molecular iodine (orthorhombic Cmca), respectively. Negative formation energies indicate thermodynamic stability with respect to decomposition into the constituent elements [24]. The use of solid I<sub>2</sub> as the iodine reference state ensures consistency with the periodic plane-wave framework [4, 25].

#### 2.4.2. Relative Phase Energetics

All total energies were normalized per CsSnI<sub>3</sub> formula unit. Energy differences  $\Delta E_e^{\text{R}_0}$  were defined relative to the lowest-energy phase [4, 1]. Within the present static-lattice framework, the yellow orthorhombic  $\delta$  phase is identified as the lowest-energy configuration and therefore represents the thermodynamic ground state. The perovskite-derived  $\alpha$ ,  $\beta$ , and  $\gamma$  phases lie higher in energy and are thus classified as metastable with respect to the  $\delta$  phase.

#### 2.4.3. Temperature-Dependent Stability Considerations

The present analysis does not include finite-temperature contributions such as vibrational free energy and configurational entropy, which are known to play important roles in stabilizing higher-symmetry perovskite phases at elevated temperatures [4, 26]. Experimental observations indicate that the  $\gamma$ -phase is typically stable below 351 K, while the  $\alpha$ - and  $\beta$ -phases require temperatures exceeding 425 K [11, 8]. A comprehensive description of temperature-dependent phase stability would require explicit calculation of phonon frequencies and free energies using density functional perturbation theory or molecular dynamics simulations [27], which is deferred to future work.

### 2.5. Correction of Band-Gap Underestimation: PBE+U Approach

Semilocal exchange–correlation functionals such as PBE

systematically underestimate band gaps of semiconductors due to self-interaction errors and the absence of the derivative discontinuity in the exchange–correlation potential [28]. To mitigate this deficiency, the DFT+U formalism was employed using the rotationally invariant Dudarev approach [29]. On-site Hubbard corrections were applied to the Sn-5s and I-5p orbitals, which dominate the electronic states near the band edges in CsSnI<sub>3</sub>. The Hubbard parameters were calibrated using the  $\gamma$  phase as a reference, yielding  $U_{\text{Sn-5s}} = 3.29$  eV and  $U_{\text{I-5p}} = 4.29$  eV. These values were subsequently applied uniformly to all CsSnI<sub>3</sub> polymorphs, ensuring that differences in band-gap values arise from intrinsic structural variations rather than parameter tuning. For applications requiring highly accurate band gaps, higher-level approaches such as many-body perturbation theory within the GW approximation [30, 31] are generally recommended.

### 2.6. Electronic Structure Calculations

Electronic band structures and total and partial densities of states (TDOS/PDOS) were calculated for all fully optimized CsSnI<sub>3</sub> polymorphs. Band structures were evaluated along high-symmetry paths of the corresponding Brillouin zones following standard conventions [32]. The electronic band gap was defined as the energy difference between the conduction-band minimum (CBM) and the valence-band maximum (VBM). Semilocal PBE calculations were employed to analyze qualitative features of the electronic structure, while DFT+U calculations refine the band-gap values.

### 2.7. Optical Properties

Optical properties were evaluated at the DFT+U level within the independent-particle approximation by computing the frequency-dependent complex dielectric function,  $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ . The imaginary part  $\epsilon_2(\omega)$  was obtained from inter-band transition matrix elements between occupied and unoccupied Kohn–Sham states, while the real part  $\epsilon_1(\omega)$  was derived via the Kramers–Kronig relation. Key optical descriptors, including the absorption coefficient, refractive index, extinction coefficient, optical conductivity, reflectivity, and energy-loss function, were obtained using standard linear-response relations [33]. In CsSnI<sub>3</sub>, the exciton binding energy has been experimentally determined to be approximately 18 meV [34], which is relatively small compared to thermal energy at room temperature (26 meV). Consequently, excitonic effects are not expected to qualitatively alter the optical absorption trends. For quantitative modeling of excitonic features, solution of the Bethe–Salpeter equation would be required [35, 36].

## 3. RESULTS AND DISCUSSION

The CASTEP-based first-principles results for CsSnI<sub>3</sub> are

presented following a consistent and hierarchical workflow: (i) numerical convergence validation, (ii) optimized crystal structures and lattice distortions, (iii) formation energies and relative phase stability, (iv) electronic structure analysis at the PBE level, (v) band-gap-corrected electronic structure using DFT+U, and (vi) optical properties derived from the DFT+U dielectric response [17, 19, 1]. This workflow ensures that reported trends arise primarily from intrinsic structural differences among polymorphs rather than numerical artifacts.

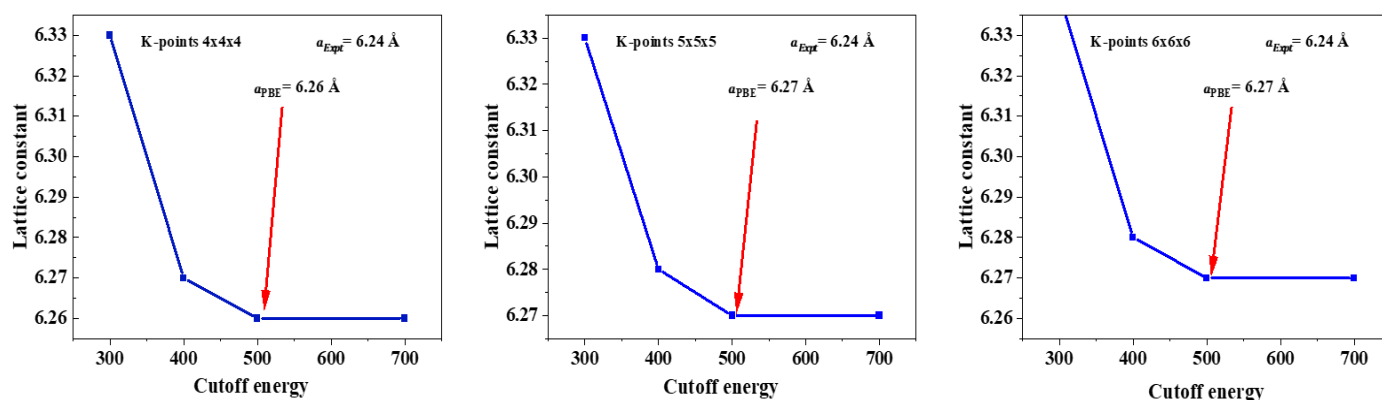
### 3.1. Numerical Convergence of Lattice Constant

Convergence tests were performed using the cubic  $\alpha$ -phase of CsSnI<sub>3</sub> as a benchmark reference structure [8, 21]. Figure 1 illustrates the convergence behavior of the equilibrium lattice constant as a function of plane-wave kinetic-energy cutoff for different Monkhorst–Pack k-point meshes [22]. At relatively low cutoff energies (300–400 eV), noticeable variations in the optimized lattice constant are observed. With increasing cutoff energy, the lattice constant rapidly

stabilizes and becomes essentially invariant beyond 500 eV for all tested k-point grids. Based on these results, a plane-wave kinetic-energy cutoff of 500 eV was adopted for all subsequent calculations [17, 4, 21].

### 3.2. Optimized Crystal Structures, Lattice Parameters, and Distortions

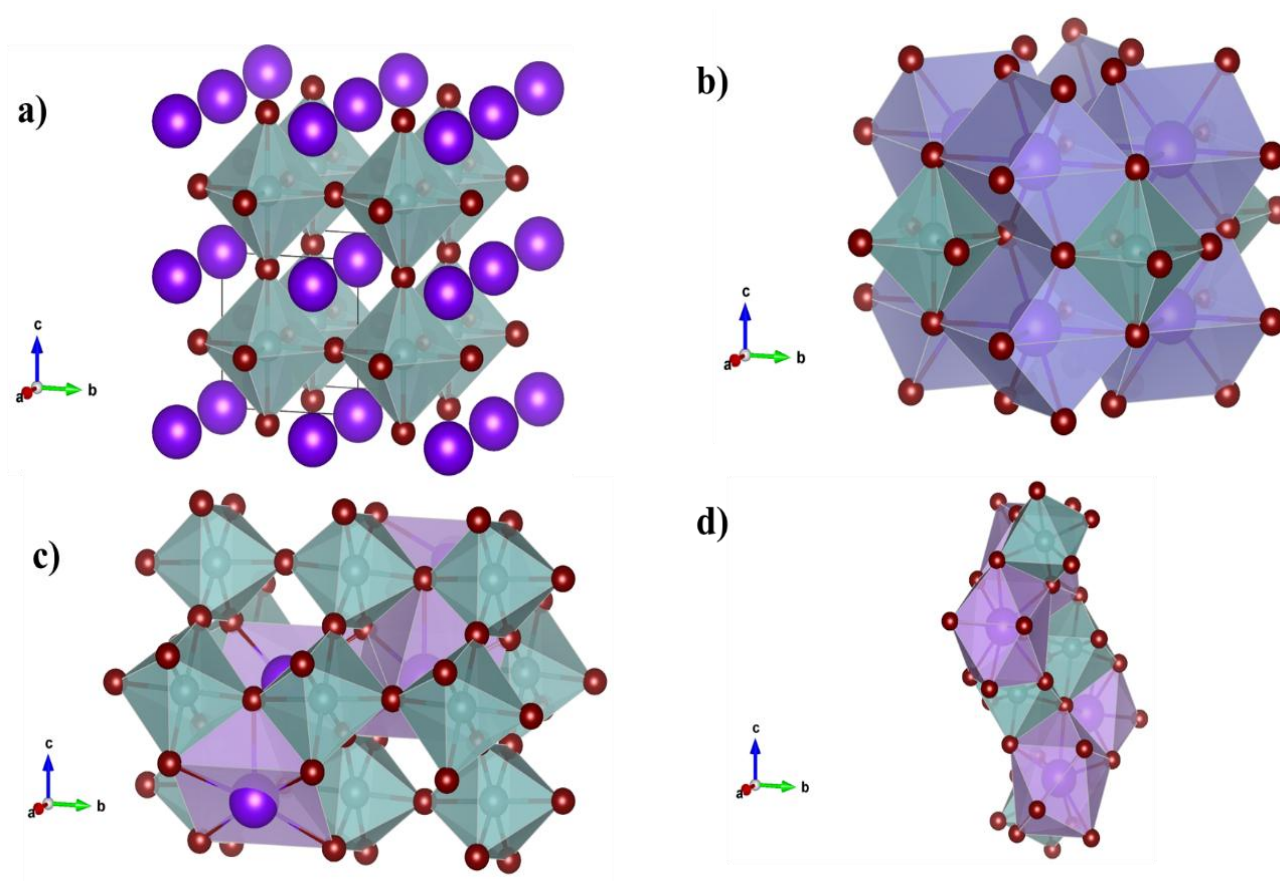
The optimized lattice parameters of the  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -phases of CsSnI<sub>3</sub> obtained from CASTEP–PBE calculations are summarized in Table 1, together with representative experimental lattice constants for comparison. The calculated lattice parameters show consistent phase-dependent trends and reasonable agreement with previous reports, with the slight overestimation of lattice constants being characteristic of the PBE functional [19]. Representative fully optimized crystal structures of the four polymorphs are shown in Figure 2. For the high-symmetry  $\alpha$ -cubic phase, the optimized lattice constant is slightly larger than the experimental value, consistent with the well-known tendency of the PBE functional to overestimate equilibrium volumes in solids [19].



**Fig. 1.** Convergence of the optimized lattice constant of cubic  $\alpha$ -CsSnI<sub>3</sub> as a function of plane-wave kinetic-energy cutoff for Monkhorst–Pack k-point meshes of 4×4×4, 5×5×5, and 6×6×6. The selected converged cutoff energy (500 eV) is indicated for reference.

**Table 1.** Optimized lattice parameters of CsSnI<sub>3</sub> polymorphs from CASTEP–PBE calculations, with experimental values shown for comparison. The  $\alpha$  phase is stable only at elevated temperatures (>430 K).

| Phase                      | a (Å)   | b (Å)   | c (Å)   | Source    |
|----------------------------|---------|---------|---------|-----------|
| $\alpha$ (Cubic)           | 6.27    | 6.27    | 6.27    | This work |
| $\beta$ (Tetragonal)       | 8.82    | 8.82    | 6.30    | This work |
| $\gamma$ (Orth., black)    | 8.87    | 12.66   | 8.73    | This work |
| $\delta$ (Orth., yellow)   | 10.78   | 4.83    | 18.15   | This work |
| <i>Experimental values</i> |         |         |         |           |
| $\alpha$ (Cubic)           | 6.2057  | 6.2057  | 6.2057  | Expt. [8] |
| $\beta$ (Tetragonal)       | 8.7182  | 8.7182  | 6.1908  | Expt. [8] |
| $\gamma$ (Orth., black)    | 8.6885  | 12.3775 | 8.6384  | Expt. [8] |
| $\delta$ (Orth., yellow)   | 10.3500 | 4.7632  | 17.6840 | Expt. [8] |



**Fig. 2.** Fully optimized crystal structures of  $\text{CsSnI}_3$  polymorphs obtained from CASTEP–PBE calculations: (a)  $\alpha$  (cubic), (b)  $\beta$  (tetragonal), (c)  $\gamma$  (orthorhombic, black), and (d)  $\delta$  (orthorhombic, yellow).

Upon symmetry lowering to the  $\beta$ -tetragonal phase, anisotropic lattice distortion emerges (with  $c \neq a = b$ ), driven by octahedral tilting of the  $\text{SnI}_6$  framework. This distortion becomes more pronounced in the orthorhombic  $\gamma$  phase, which exhibits enhanced lattice anisotropy and stronger octahedral tilting while preserving the corner-sharing  $\text{SnI}_6$  connectivity characteristic of perovskite-derived structures. In contrast, the orthorhombic  $\delta$  phase adopts a non-perovskite, edge-sharing  $\text{SnI}_6$  octahedral network, resulting in a distinct bonding topology that reduces electronic connectivity and significantly modifies the electronic structure [8, 9].

### 3.3. Formation Energy and Relative Phase Stability

#### 3.3.1. Formation Energy Analysis

The calculated formation energies for all  $\text{CsSnI}_3$  polymorphs, obtained using Eq. (1), are summarized in Table 2. All four phases exhibit negative formation energies, confirming thermodynamic stability with respect to decomposition into the constituent elements. The  $\delta$  phase shows the most negative formation energy ( $E^f = -2.663$  eV/f.u.), followed closely by the  $\gamma$  ( $-2.636$  eV/f.u.),  $\beta$  ( $-2.634$  eV/f.u.), and  $\alpha$

( $-2.628$  eV/f.u.) phases. The small energy differences among polymorphs (8–35 meV per formula unit) are consistent with experimentally observed temperature-dependent phase transitions [11, 8].

#### 3.3.2. Relative Phase Energetics and Metastability

Within the present static-lattice framework, the yellow orthorhombic  $\delta$  phase emerges as the thermodynamic ground state. The perovskite-derived  $\alpha$ ,  $\beta$ , and  $\gamma$  phases lie 28–35 meV/f.u. higher in energy, classifying them as metastable with respect to the  $\delta$  phase. Among the perovskite polymorphs, the  $\gamma$  phase is energetically most favorable, followed closely by  $\beta$  (energy difference  $\sim 1$  meV/f.u.), and then  $\alpha$ . The near-degeneracy between the  $\beta$  and  $\gamma$  phases indicates a highly competitive phase landscape that is sensitive to synthesis conditions and thermal effects. This energetic ordering is consistent with previous first-principles studies [4, 21] and reflects the progressive stabilization associated with octahedral tilting and structural distortion within the corner-sharing  $\text{SnI}_6$  framework. Although the black perovskite phases are metastable, they can be kinetically stabilized under suitable synthesis and processing conditions.

**Table 2.** Formation energies and relative phase stability of CsSnI<sub>3</sub> polymorphs calculated at the CASTEP–PBE level. Formation energies ( $E^f$ ) are referenced to elemental Cs (bcc), Sn ( $\beta$ -Sn), and solid I<sub>2</sub> (orthorhombic Cmca). All energies are per formula unit (f.u.).

| Phase                   | $Z^a$ | $E_{\text{total}}$ (eV/f.u.) | $E_f$ (eV/f.u.) | $\Delta E_{\text{rel}}$ (meV/f.u.) |
|-------------------------|-------|------------------------------|-----------------|------------------------------------|
| $\alpha$ (Cubic)        | 1     | −5227.711                    | −2.628          | 35.1                               |
| $\beta$ (Tetragonal)    | 2     | −5227.717                    | −2.634          | 28.9                               |
| $\gamma$ (Black Orth.)  | 4     | −5227.719                    | −2.636          | 27.6                               |
| $\delta$ (Yellow Orth.) | 4     | −5227.746                    | −2.663          | 0.0                                |

<sup>a</sup> Number of formula units per unit cell

**Table 3.** Electronic band gaps of CsSnI<sub>3</sub> polymorphs obtained using PBE and DFT+U, compared with representative literature values. A uniform set of Hubbard parameters ( $U_{\text{Sn-5s}} = 3.29$  eV,  $U_{\text{I-5p}} = 4.29$  eV) was applied to all phases.

| Phase                    | PBE (eV) | DFT+U (eV) | Literature (eV)   |
|--------------------------|----------|------------|-------------------|
| $\alpha$ (Cubic)         | 0.44     | 1.10       | 0.95–1.32 [8, 21] |
| $\beta$ (Tetragonal)     | 0.55     | 1.20       | 1.10–1.20 [8, 21] |
| $\gamma$ (Orth., black)  | 0.60     | 1.30       | 1.27–1.30 [8]     |
| $\delta$ (Orth., yellow) | 2.17     | 3.00       | 2.50–2.99 [8,10]  |

### 3.3.3. Temperature-Dependent Stability and Experimental Context

The present formation energy analysis is based on static lattice energies. Experimental observations demonstrate that phase stability in CsSnI<sub>3</sub> is strongly temperature-dependent: the  $\gamma$  phase is typically observed below 351 K, while the  $\beta$  and  $\alpha$  phases require temperatures exceeding 425 K for thermodynamic stabilization [11, 8]. The small energy differences calculated here (27–35 meV/f.u.) are comparable to thermal energies at elevated temperatures, suggesting that vibrational and entropic effects play crucial roles in determining phase stability under experimental conditions. A comprehensive description of temperature-dependent phase behavior would require explicit calculation of phonon frequencies using DFPT or molecular dynamics simulations [27, 26], which is beyond the scope of the present comparative study.

## 3.4. Electronic Structure

The electronic band structures together with the corresponding total and partial densities of states (DOS/PDOS) for all CsSnI<sub>3</sub> polymorphs are presented in Figures 3 and 4, obtained from semilocal PBE and band-gap-corrected DFT+U calculations, respectively. The associated band-gap values at both levels of theory, along with representative literature data, are summarized in Table 3.

At the semilocal PBE level, all polymorphs are predicted to be semiconducting; however, the absolute band-gap values are significantly underestimated, as expected for GGA functionals [19, 28]. For the perovskite-derived  $\alpha$ -,  $\beta$ -, and  $\gamma$ -phases, DOS/PDOS analysis reveals that the valence-

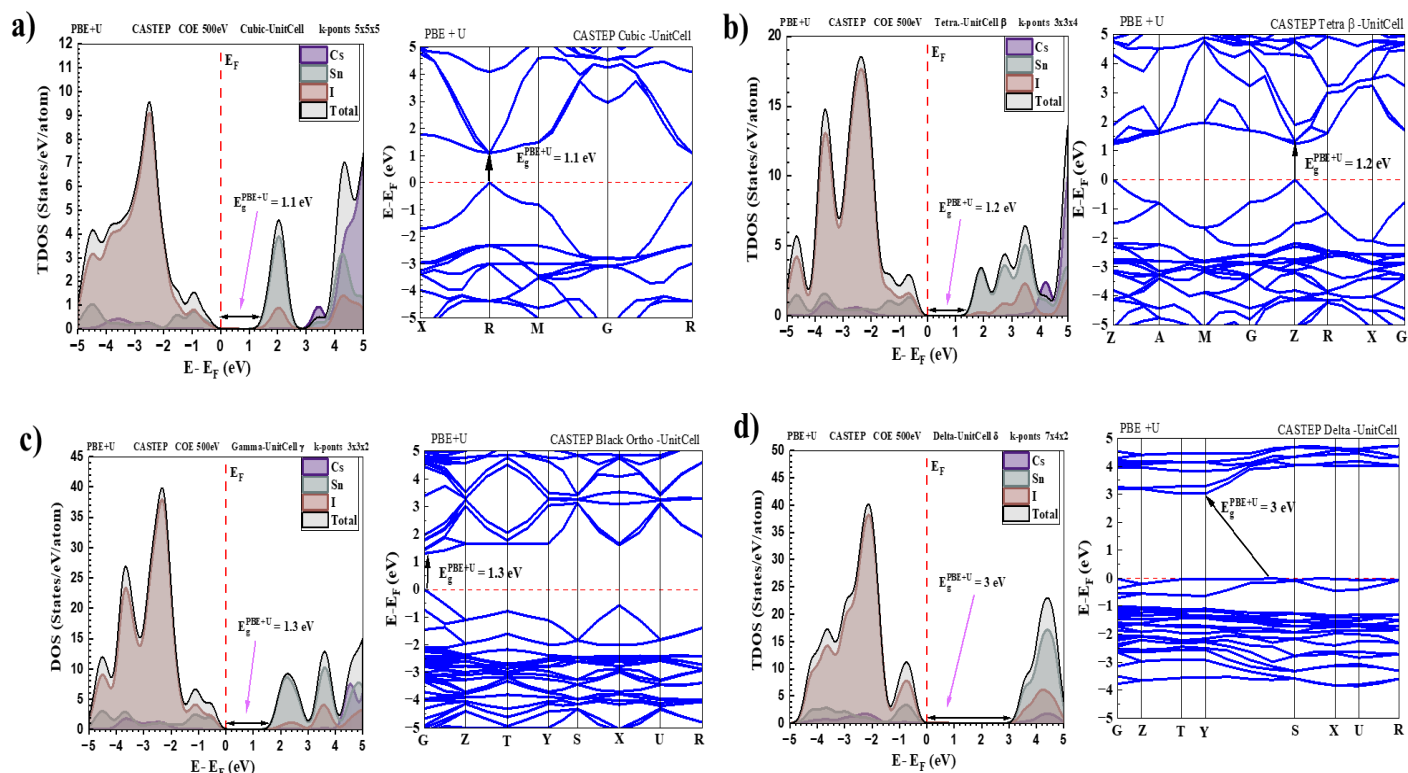
band maximum (VBM) is dominated by I-5p states strongly hybridized with Sn-5s orbitals, whereas the conduction-band minimum (CBM) primarily originates from Sn-5p states. This band-edge composition is characteristic of tin-halide perovskites and is commonly associated with relatively dispersive band edges that are favorable for charge-carrier transport [8, 38]. Contributions from Cs-derived states remain far from the band edges, indicating a largely ionic role for the A-site cation.

### 3.4.1. Band-Gap Correction Using DFT+U

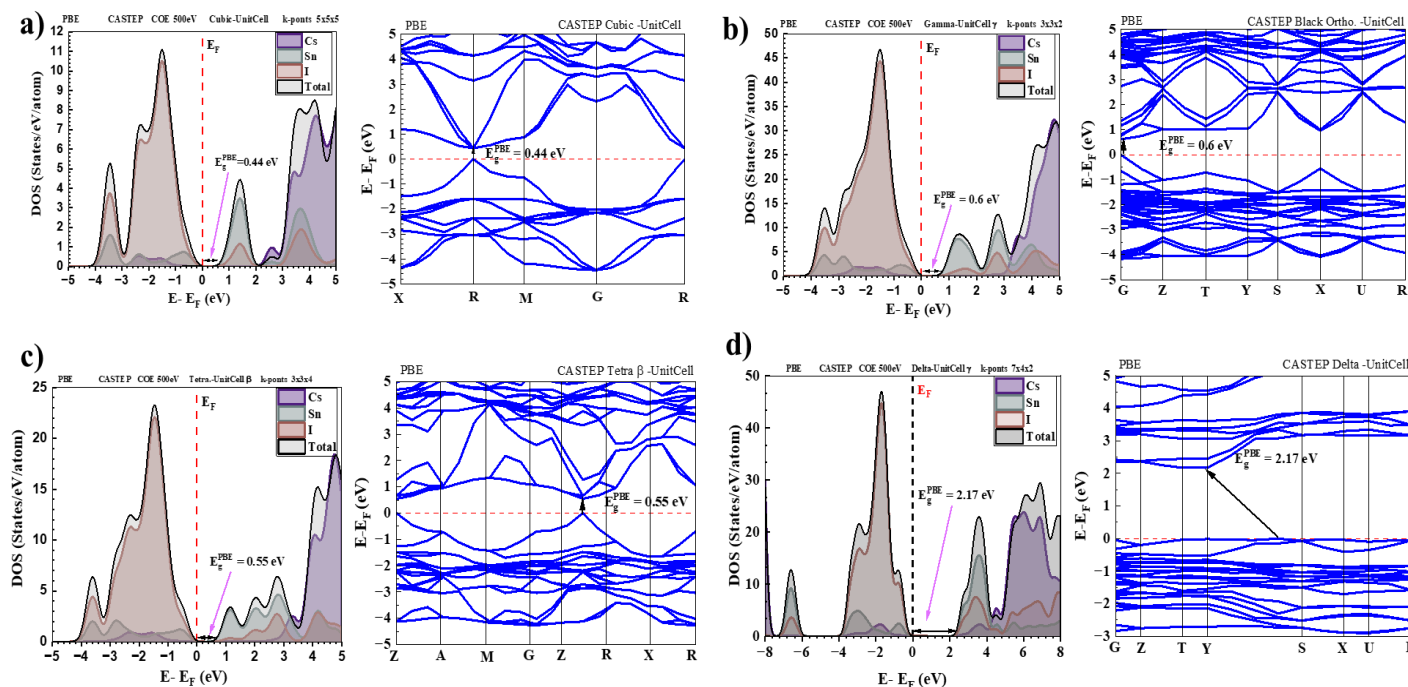
To improve band-gap estimation, the DFT+U approach described in Section 2.5 was employed. The Hubbard parameters were calibrated using the  $\gamma$  phase, yielding  $U_{\text{Sn-5s}} = 3.29$  eV and  $U_{\text{I-5p}} = 4.29$  eV, and applied uniformly to all CsSnI<sub>3</sub> polymorphs. The calculated band gaps are 1.10 eV ( $\alpha$ ), 1.20 eV ( $\beta$ ), 1.30 eV ( $\gamma$ ), and 3.00 eV ( $\delta$ ). The  $\gamma$  phase exhibits excellent agreement with experimental values (1.27–1.30 eV), confirming the validity of the adopted Hubbard parameters. In contrast, the  $\delta$  phase shows a significantly larger band gap due to its non-perovskite structure and reduced electronic connectivity.

## 3.5. Optical Properties at the DFT+U Level

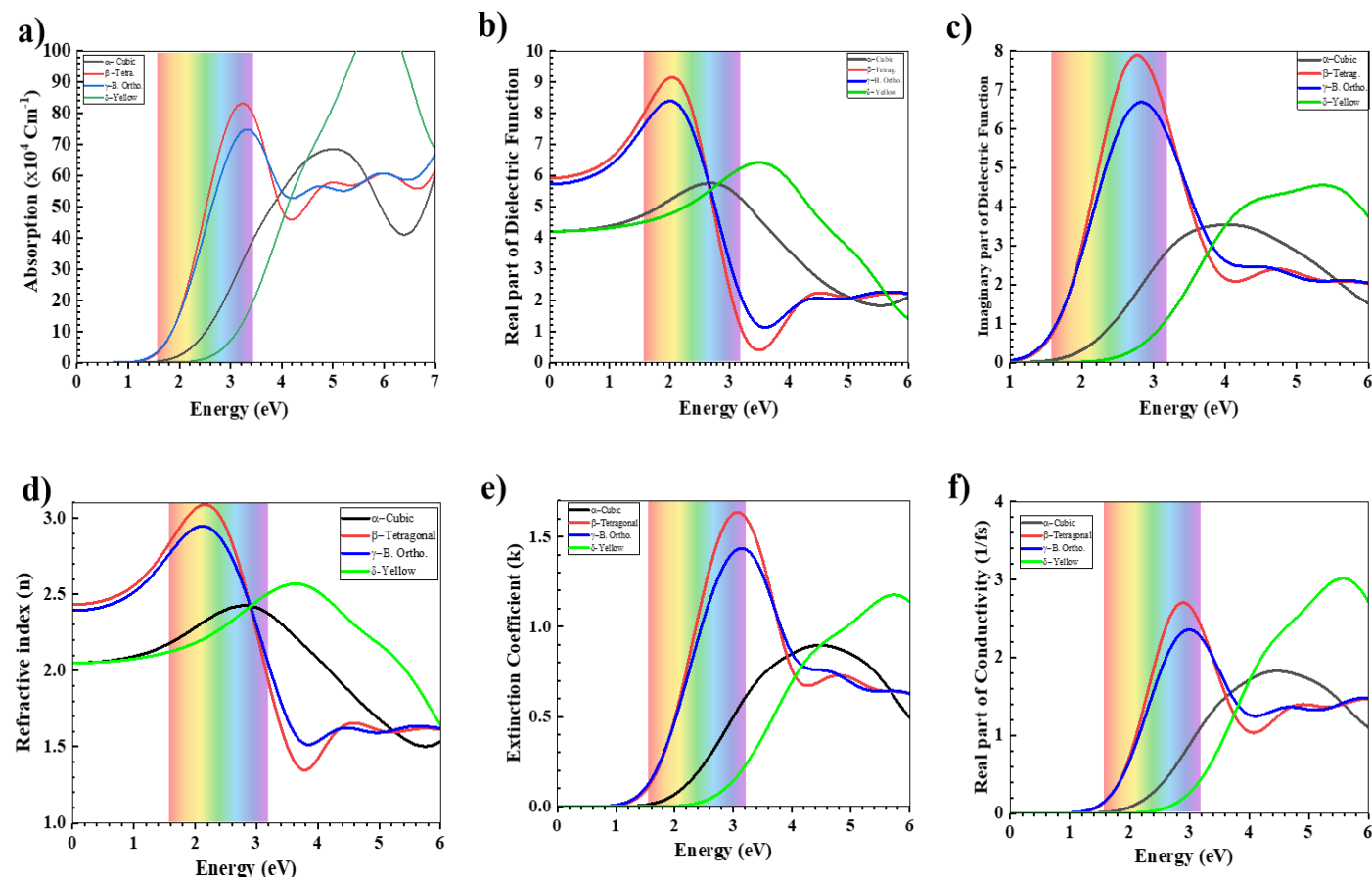
The optical properties of the CsSnI<sub>3</sub> polymorphs were investigated at the DFT+U level through evaluation of the frequency-dependent complex dielectric function,  $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$  [33]. Figure 5 summarizes the resulting optical spectra, with the shaded region highlighting the visible spectral range relevant for photovoltaic applications.



**Fig. 3.** CASTEP–PBE electronic band structures and corresponding total and partial densities of states (DOS/PDOS) for  $\text{CsSnI}_3$  polymorphs: (a)  $\alpha$  (cubic), (b)  $\beta$  (tetragonal), (c)  $\gamma$  (orthorhombic, black), and (d)  $\delta$  (orthorhombic, yellow). The Fermi level is set to 0 eV.



**Fig. 4.** CASTEP–DFT+U electronic band structures and corresponding DOS/PDOS for  $\text{CsSnI}_3$  polymorphs: (a)  $\alpha$  (cubic), (b)  $\beta$  (tetragonal), (c)  $\gamma$  (orthorhombic, black), and (d)  $\delta$  (orthorhombic, yellow). A uniform set of Hubbard parameters ( $U_{\text{Sn}-5s} = 3.29$  eV,  $U_{\text{I}-5p} = 4.29$  eV) was applied. The Fermi level is set to 0 eV.



**Fig. 5.** DFT+U optical properties of CsSnI<sub>3</sub> polymorphs from the complex dielectric response: (a) absorption coefficient, (b) real part  $\epsilon_1(\omega)$ , (c) imaginary part  $\epsilon_2(\omega)$ , (d) refractive index  $n(\omega)$ , (e) extinction coefficient  $k(\omega)$ , and (f) optical conductivity. The shaded region indicates the visible spectral range.

The perovskite-derived  $\alpha$ ,  $\beta$ , and  $\gamma$  phases exhibit pronounced optical absorption within the visible spectral range, with the  $\gamma$  phase displaying the strongest and broadest visible-light absorption, with peak absorption coefficients exceeding  $10^5 \text{ cm}^{-1}$  [8, 5]. The real part of the dielectric function,  $\epsilon_1(\omega)$ , reveals a strong low-energy dielectric response for the perovskite-derived phases, with the  $\gamma$  phase exhibiting the largest static dielectric screening [12]. The imaginary component,  $\epsilon_2(\omega)$ , exhibits prominent features within the visible range for the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases, reflecting strong interband optical transitions.

In contrast, the yellow orthorhombic  $\delta$  phase exhibits weak visible-light absorption, low optical conductivity, and reduced dielectric response. This behavior originates from its larger band gap and the more localized electronic states associated with the edge-sharing SnI<sub>6</sub> framework. These results highlight that thermodynamic stability alone does not guarantee photovoltaic suitability; instead, octahedral connectivity, electronic delocalization, and band-edge dispersion play decisive roles in governing optical performance [1, 9, 21]. Overall, the  $\gamma$  phase uniquely combines strong visible-light absorption with enhanced dielectric screening and favorable optical conductivity,

reinforcing its suitability as a lead-free CsSnI<sub>3</sub> absorber for optoelectronic and photovoltaic applications.

## 4. CONCLUSIONS

A comprehensive first-principles investigation of the structural, energetic, electronic, and optical properties of the  $\alpha$  (cubic),  $\beta$  (tetragonal),  $\gamma$  (black orthorhombic), and  $\delta$  (yellow orthorhombic) polymorphs of CsSnI<sub>3</sub> has been performed within a consistent CASTEP-based DFT framework. Systematic geometry optimizations and formation energy analyses identify the yellow orthorhombic  $\delta$  phase as the thermodynamically most stable configuration, with a formation energy of  $-2.663 \text{ eV}$  per formula unit with respect to the constituent elements. The perovskite-derived  $\alpha$ ,  $\beta$ , and  $\gamma$  phases are metastable yet energetically competitive (lying 28–35 meV/f.u. higher in energy), reflecting the delicate phase competition inherent to tin-based halide perovskites. Electronic-structure analysis reveals pronounced phase-dependent trends governed by symmetry lowering, octahedral tilting, and the connectivity of the SnI<sub>6</sub> framework. The application of a consistent DFT+U approach,

with Hubbard parameters calibrated using the  $\gamma$  phase ( $USn_{-s} = 3.29$  eV and  $UI_{-sp} = 4.29$  eV) and applied uniformly across all polymorphs, significantly improves band-gap estimation while preserving the intrinsic phase-dependent electronic trends. The resulting DFT+U band gaps are 1.10 eV ( $\alpha$ ), 1.20 eV ( $\beta$ ), 1.30 eV ( $\gamma$ ), and 3.00 eV ( $\delta$ ). The excellent agreement obtained for the  $\gamma$  phase with experimental values (1.27–1.30 eV) validates the adopted methodology. Optical-property calculations further demonstrate that the perovskite-derived  $\alpha$ ,  $\beta$ , and  $\gamma$  phases exhibit strong visible-light absorption and enhanced dielectric response, in contrast to the wide-gap and optically inactive  $\delta$  phase. Among the investigated structures, the  $\gamma$  phase emerges as the most promising, combining a near-optimal band gap with favorable band-edge dispersion, strong optical absorption exceeding  $10^5$  cm<sup>-1</sup>, and enhanced dielectric screening. Overall, this work establishes a computationally efficient and internally consistent framework for evaluating phase-dependent properties in CsSnI<sub>3</sub> polymorphs and provides a validated foundation for subsequent high-accuracy electronic-structure calculations and device-oriented modeling aimed at advancing lead-free perovskite technologies.

## ABBREVIATIONS

|               |                                                            |
|---------------|------------------------------------------------------------|
| <b>CBM</b>    | Conduction Band Minimum                                    |
| <b>DFT</b>    | Density Functional Theory                                  |
| <b>DFPT</b>   | Density Functional Perturbation Theory                     |
| <b>DOS</b>    | Density of States                                          |
| <b>GGA</b>    | Generalized Gradient Approximation                         |
| <b>MP</b>     | Monkhorst–Pack                                             |
| <b>PBE</b>    | Perdew–Burke–Ernzerhof                                     |
| <b>PBE+U</b>  | Generalized Gradient Approximation with Hubbard Correction |
| <b>PDOS</b>   | Projected Density of States                                |
| <b>SOC</b>    | Spin–Orbit Coupling                                        |
| <b>USP</b>    | Ultrasoft Pseudopotentials                                 |
| <b>VBM</b>    | Valence Band Maximum                                       |
| <b>CASTEP</b> | Cambridge Sequential Total Energy Package                  |

## DECLARATIONS

### Ethical Approval

We affirm that this manuscript is an original work, has not been previously published, and is not currently under consideration for publication in any other journal or conference proceedings. All authors have reviewed and approved the manuscript, and the order of authorship has been mutually agreed upon.

### Funding

Not Applicable

## Availability of data and material

All of the data obtained or analyzed during this study is included in this paper.

## Conflicts of Interest

The authors declare that they have no financial or personal interests that could have influenced the research and findings presented in this paper. The authors alone are responsible for the content and writing of this article.

## Author's contribution statement

All authors have contributed equally to the research and preparation of this work.

## Data availability statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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The computations in this work were performed using local computational resources.

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