

Electronic Structure of Cubic CsSnI₃: A First-Principles Assessment and Implications for Lead-Free Perovskite

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Abstract:

Lead-free tin-halide perovskites are promising candidates for optoelectronic applications, motivating a detailed understanding of their electronic structure. This study investigates cubic CsSnI₃ using density functional theory within a semilocal Perdew–Burke–Ernzerhof-type generalized-gradient approximation, implemented in Quantum Espresso. The band structure along $X \rightarrow R \rightarrow M \rightarrow \Gamma \rightarrow R$ indicates a direct band gap of approximately 0.5 eV, with both the valence-band maximum and conduction-band minimum located at R. The projected density of states shows predominantly Iodine 5p contributions in the valence-band region and Tin 5s/5p contributions in the conduction-band region, with comparatively little Cs contribution near the Fermi level. Band-edge dispersion suggests potentially favourable charge transport. Overall, the results support the semiconducting character of cubic CsSnI₃ and provide a qualitative electronic-structure basis for its relevance to lead-free optoelectronics.

Keywords: CsSnI₃; lead-free perovskite; quantum dots; density functional theory; Quantum ESPRESSO; BURAI; band structure; density of states; band gap; optoelectronics.

1. Introduction

Metal-halide perovskites have attracted considerable attention as promising materials for optoelectronic applications owing to their strong optical absorption, tunable electronic structures, and favourable charge-transport properties. These characteristics make them attractive candidates for photovoltaic devices, light-emitting diodes, and other next-generation optoelectronic technologies [1]. Despite the remarkable progress achieved with lead-based perovskites, concerns regarding lead toxicity and potential environmental contamination have stimulated extensive research into alternative compositions with reduced environmental impact. In this context, lead-free metal-halide perovskites have emerged as an important class of materials, with tin-based compounds receiving particular attention because Sn²⁺ can partially reproduce the electronic characteristics of Pb²⁺. Among these materials, all inorganic cesium tin iodide (CsSnI₃) is especially interesting because of its composition-dependent structural and

optoelectronic properties [2]. In its ideal ABX_3 perovskite structure, Cs occupies the A site, Sn the B site, and I the halide site. The black perovskite polymorph exhibits a narrow band gap and strong absorption extending into the near-infrared region, making $CsSnI_3$ a potential candidate for photovoltaic and light-emitting applications. However, its technological implementation remains challenging because of the susceptibility of Sn^{2+} to oxidation into Sn^{4+} , together with structural and phase instabilities under ambient and operating conditions.

The structural stability and optoelectronic response of $CsSnI_3$ are closely associated with its crystallographic symmetry and polymorphic nature [3]. Depending on temperature and environmental conditions, $CsSnI_3$ can adopt distinct structural phases, including black perovskite polymorphs and a yellow non-perovskite phase. These phases differ significantly in their structural connectivity and electronic properties, highlighting the importance of establishing an appropriate structural model when investigating the material's fundamental characteristics. Experimental investigations have identified the black perovskite phase as a direct-band-gap semiconductor with a room-temperature band gap of approximately 1.3 eV, although the reported value depends on the phase, measurement conditions, and experimental methodology. A detailed understanding of the electronic band structure and density of states is therefore essential for identifying the orbital contributions to the valence-band maximum and conduction-band minimum, assessing the nature of the electronic transitions, and establishing relationships between crystal structure and optoelectronic performance. First-principles calculations based on density functional theory (DFT) provide a valuable framework for such investigations because they enable the systematic analysis of electronic states and their dispersion throughout reciprocal space. Nevertheless, the reliability of the predicted properties depends on the structural configuration, exchange–correlation functional, treatment of relativistic effects, and other computational parameters. Against this background, the present study investigates the electronic structure of cubic $CsSnI_3$ using density functional theory as implemented in the Quantum ESPRESSO computational package [4,5]. The principal objectives are to establish the structural model and computational framework, analyse the calculated electronic band structure and density of states, identify the principal electronic states contributing to the band edges, and compare the resulting numerical estimates with established experimental and theoretical findings. Attention is given to understanding the differences between calculated and literature-reported band-gap values in terms of the structural model and the limitations of the adopted computational approach.

2. Computational Methodology

2.1 Density Functional Theory framework

Within density functional theory, the ground-state electron density is used in place of the full many-body wavefunction to describe an interacting electron system. Its formal basis is provided by the Hohenberg–Kohn theorems, whereas the Kohn–Sham scheme recasts the many-electron problem as a set of effective one-electron equations solved self-consistently. In the present methodology, the principal computational elements are the exchange–correlation approximation, Kohn–Sham orbitals and electron density, pseudopotentials, Brillouin-zone sampling, plane-wave energy cutoffs, and numerical convergence tests.

The electronic-structure calculations were performed using a semilocal Perdew–Burke–Ernzerhof-type generalized-gradient approximation.

2.2 Structural model and CIF construction

The complementary study constructs a cubic CsSnI_3 model through a crystallographic information file and transfers the structural information to a Quantum ESPRESSO input. The model uses a simple-cubic Bravais lattice ($\text{ibrav} = 1$), five atoms per unit cell and three atomic species. The lattice parameter has been taken as $a = 6.28623 \text{ \AA}$. The atomic positions used in the input are expressed in ångström coordinates.

Parameter	Specification
Crystal structure	Cubic perovskite; simple cubic Bravais lattice
Lattice parameter, a	$6.28623 \text{ \AA}$
Atoms per unit cell	5 (1 Cs + 1 Sn + 3 I)
Atomic types	3
Cs pseudopotential	Cs.pbe-spn-rrkjus_psl.1.0.0.UPF
I pseudopotential	I.pbe-dn-rrkjus_psl.1.0.0.UPF
Sn pseudopotential	Sn.pbe-dn-rrkjus_psl.1.0.0.UPF
SCF wavefunction cutoff	75 Ry
SCF charge-density cutoff	375 Ry
SCF k-point mesh	$7 \times 7 \times 7$
SCF convergence threshold	1×10^{-6}
Smearing	Fermi–Dirac; degauss = 0.01
Band-structure path	$X \rightarrow R \rightarrow M \rightarrow \Gamma \rightarrow R$

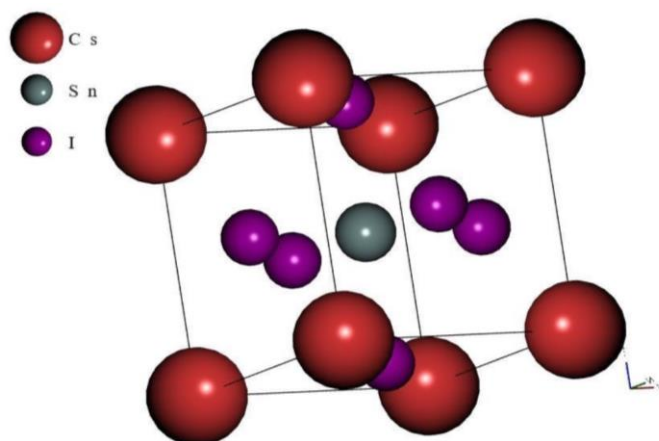


Figure 1. Cubic CsSnI_3 structure (As per the Quantum Espresso input File)

3. Results and Discussion

3.1 Electronic band structure

After structural optimization and SCF calculation, the band structure was evaluated along the high-symmetry path $X \rightarrow R \rightarrow M \rightarrow \Gamma \rightarrow R$. The energy scale was referenced to the Fermi level at 0 eV. The obtained band plot showed the valence and conduction bands approaching each other at the R symmetry point. Thus it is clear from the figure 2 that the prepared CsSnI_3 structure is a direct band gap material having a band gap of approximately 0.5 eV, with both the Valence Band Maximum and Conduction Band Minimum located at R.

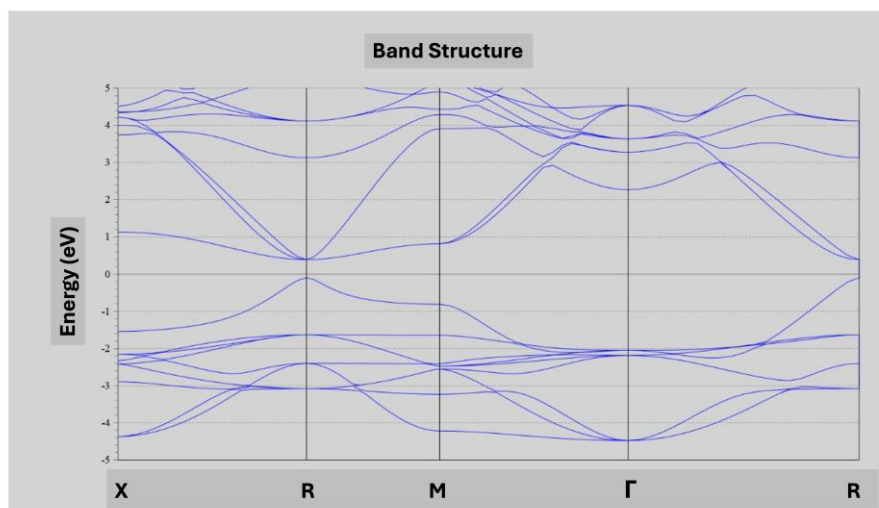


Figure 2. Calculated band structure of cubic CsSnI_3 along $X \rightarrow R \rightarrow M \rightarrow \Gamma \rightarrow R$

The dispersion of the bands near the band edges provides qualitative insight into carrier transport. The relatively pronounced band dispersion around the R point suggests, qualitatively, low carrier effective masses and, consequently potentially favourable charge-transport behaviour. The predicted band gap is considerably lower than the optical gap of approximately 1.2–1.3 eV reported for black CsSnI_3 . This discrepancy is consistent with the established tendency of semilocal DFT to underestimate semiconductor band gaps. Experimentally, CsSnI_3 thin films have been reported to exhibit a direct band gap of approximately 1.3 eV at room temperature.

3.2 Density of states and orbital contributions

The total and projected densities of states (DOS and PDOS) complement the band-structure analysis by describing the energy distribution and orbital character of the electronic states. In the reported calculation, the Fermi level is referenced to 0 eV, and the DOS exhibits a semiconducting profile with an apparent energy separation of approximately 1.2 eV.

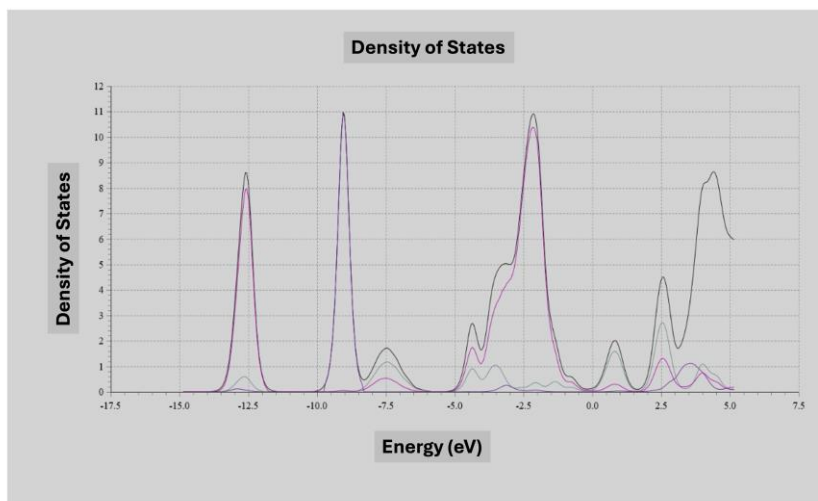


Figure 3. Total and orbital-projected densities of states of CsSnI_3

The PDOS indicates that iodine 5p orbitals make the predominant contribution to the valence-band region, particularly over the energy range from approximately -12.5 to -2.5 eV. By contrast, the conduction-band region is composed mainly of Sn 5s and 5p states. The contribution of Cs near the Fermi level is comparatively small, supporting its predominantly structural role rather than direct participation in the band-edge states. The distinct peaks in the DOS correspond to localized or strongly weighted electronic states that may affect charge-transport processes and optical transitions. The band-structure gap of approximately 0.5 eV and the DOS-derived separation of approximately 1.2 eV should not be regarded as two distinct intrinsic band gaps without first considering the differences between the corresponding numerical procedures. The band-structure calculation evaluates electronic states along selected high-symmetry directions, whereas the DOS integrates states throughout the Brillouin zone. Moreover, the broadening or smearing used to construct the DOS can modify the apparent onset of occupied and unoccupied states, while finite k-point sampling and band interpolation may influence the visually estimated band edges. The DOS alone also cannot establish whether the gap is direct or indirect, therefore, band structure becomes important here, although due to the limitations in computation, bandgap has been predicted at lower value than the experimentally reported value. Also, both the calculations supported the semiconducting character of CsSnI_3 .

3.3. Comparison with literature [6-8]

Quantity	Earlier literature / supplied comparison	Present supplied calculation
Crystal model	Cubic, tetragonal and orthorhombic phases are reported for CsSnI_3	Cubic perovskite
Lattice parameter	Reported DFT values around 6.25 Å in cubic calculations	6.28623 Å

Band gap	~1.2–1.3 eV optical/experimental black phase; some DFT values lower	~0.5 eV from band structure
DOS gap	—	~1.2 eV
Gap character	Direct-gap behaviour reported for black CsSnI ₃	Direct at R in the reported band path
Band-edge states	I 5p valence and Sn states near conduction edge are reported	I 5p valence; Sn 5s/5p conduction

Comparison with the published literature supports the overall electronic-structure picture obtained from the calculations, while underscoring the need for caution in interpreting the absolute band-gap value. Stoumpos et al. reported phase transitions and high carrier mobilities in tin iodide perovskites, whereas Shum et al. experimentally confirmed direct-gap behaviour and a room-temperature band gap of approximately 1.3 eV in black CsSnI₃ thin films [6-8].

5. Conclusions

This study assessed the electronic structure of cubic CsSnI₃ using density functional theory within a semilocal PBE-type generalized-gradient approximation, as implemented in Quantum ESPRESSO. For the cubic model with a lattice parameter of 6.28623 Å, the calculated band structure along X→R→M→Γ→R indicates a direct band gap of approximately 0.5 eV, with the valence-band maximum and conduction-band minimum located at R. The reported projected density of states identifies predominantly I 5p contributions in the valence-band region and Sn 5s/5p contributions in the conduction-band region, while the comparatively small Cs contribution near the Fermi level supports its mainly structural role. The dispersion near the band edges suggests potentially favourable charge transport, although this interpretation remains qualitative.

The 0.5 eV band-structure gap is smaller than the experimental optical range of 1.2–1.3 eV, consistent with the limitations of the adopted semilocal approximation and the importance of the structural model and computational treatment. The apparent DOS separation of 1.2 eV should not be interpreted as an independent intrinsic band gap or as confirmation of quantitative agreement with experiment. Rather, the difference between the two estimates remains a limitation of the present analysis, with k-point sampling, broadening and band-edge identification affecting their interpretation. Overall, the calculations support the semiconducting character of cubic CsSnI₃ and provide a qualitative basis for understanding its relevance to lead-free optoelectronics. Its practical application nevertheless remains constrained by the oxidation and phase-instability challenges.

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