



Research article

Effect of Pb-Sn substitution on the structural, electronic, optical, and thermodynamic properties of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75): A DFT study

Hala Mahammedi^{a,*}, Nahida Musayeva^b, Zeyneb Amara^c, El Hassen Amara^d

^a Department of Automation, Telecommunications and Power Engineering, Baku Engineering University, Baku, Azerbaijan

^b Application Technologies of Nanomaterials, Institute of Physics, Azerbaijan Ministry of Science and Education, H. Javid ave., 131, Baku AZ1143, Azerbaijan

^c Institute of Technology, Artificial Intelligence Laboratory for Mechanical and Civil Structures, and Soil, University Centre of Naama, P.O. Box 66, Naama 45000, Algeria

^d Laboratory Physico-Chemical of Materials, University of Laghouat, Algeria

ARTICLE INFO

Keywords:

Halide Perovskite
 $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$
 Photovoltaic
 Structural
 Electronic
 Optical properties
 Thermodynamic properties

ABSTRACT

Halide perovskites have emerged as promising materials for optoelectronic and photovoltaic applications owing to their outstanding optoelectronic properties and tunable band gaps. Among them, all-inorganic halide perovskites have attracted significant attention because their structural, electronic, and optical properties can be effectively tailored through B-site cation substitution. However, the composition-dependent behavior of intermediate Pb/Sn ratios in cubic $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ remains insufficiently explored, particularly through accurate atomic modeling of substituted configurations. In this work, the effect of partial Pb/Sn substitution on the structural, electronic, optical and thermodynamic properties of cubic $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ with Sn concentrations of $x = 0.25$ and $x = 0.75$ was systematically investigated using first-principles calculations. Ordered $2 \times 2 \times 1$ supercell models were employed to represent the Pb/Sn distribution, while density functional theory (DFT) calculations were performed using the Wu–Cohen generalized gradient approximation (WC-GGA) for structural optimization. The electronic and optical properties were further evaluated using the KTB-mBJ exchange potential. The calculated band gaps are 1.45 eV for $x = 0.25$ and 1.67 eV for $x = 0.75$, accompanied by static dielectric constants of 3.12 and 3.85, respectively. The increase in Sn concentration leads to a slight widening of the band gap and induces noticeable modifications in the optical response. Furthermore, the thermodynamic properties were analyzed within the quasi-harmonic Debye model, revealing a physically consistent temperature-dependent behavior characterized by gradual lattice softening while maintaining structural stability over the investigated temperature range. The calculated E–V curves confirm the favorable structural stability of both investigated compositions within the considered configurations. These results demonstrate that controlled Pb/Sn substitution provides an effective approach for tailoring the electronic, optical and thermal characteristics of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$. This study provides new insights into the composition-dependent properties of intermediate Pb–Sn bromide perovskites and contributes to the rational design of optimized inorganic perovskite materials for optoelectronic applications.

1. Introduction

In comparison to nuclear and fossil fuels, solar energy represents a clean and sustainable source of power. Light energy conversion technologies can be categorized into several types, among which photovoltaics combines both established and emerging approaches. Considerable

efforts have been devoted to developing efficient, stable, and reproducible normal and inverted perovskite solar cells (PSCs) and photovoltaic (PV) modules using low-cost, environmentally friendly, and large-area fabrication techniques suitable for large-scale applications in both residential and industrial sectors [1,2].

In recent years, halide perovskite solar cells (HPSCs), with the

* Corresponding author.

E-mail addresses: hmahammedi@std.beu.edu.az (H. Mahammedi), nmusayeva@physics.science.az (N. Musayeva), amara.Zeyneb@cuniv-naama.dz (Z. Amara), h.amara@lagh-univ.dz (E.H. Amara).

<https://doi.org/10.1016/j.nxmte.2026.103119>

Received 10 May 2026; Received in revised form 5 August 2026; Accepted 7 August 2026

Available online 11 August 2026

2949-8228/© 2026 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

general chemical formula ABX_3 , have attracted significant attention due to their excellent light-harvesting properties over a broad spectral range, making them promising candidates for photovoltaic and optoelectronic applications [3]. Their solution-processable nature, which does not require rare or expensive elements, enables cost-effective and scalable fabrication [4,5]. As a result, perovskite materials have rapidly emerged as highly efficient light absorbers for next-generation photovoltaic technologies [6–10].

In addition, organic solar cells have gained considerable interest due to their advantages such as mechanical flexibility, lightweight structure, low cost, and ease of solution processing [11–14]. All-inorganic perovskites have also attracted increasing attention because of their superior thermal stability compared to hybrid counterparts [15–17]. However, many bromide-based perovskite systems still suffer from instability issues under ambient conditions, which limits their practical applications [18–21].

The $CsPb_{1-x}Sn_xBr_3$ system has recently attracted attention as a promising lead–tin mixed perovskite due to its tunable optoelectronic properties. Tin (Sn) and lead (Pb), belonging to the same group in the periodic table, exhibit similar electronic configurations, making Sn a suitable partial substitute for Pb in perovskite structures. The selection of the $CsPb_{1-x}Sn_xBr_3$ system is motivated by the possibility of tailoring its electronic and optical properties through partial Pb/Sn substitution while preserving the structural simplicity and superior thermal stability of the all-inorganic cubic perovskite framework. In addition, partial substitution of Pb with Sn provides an effective strategy for reducing Pb content and engineering the band gap, making this system an attractive platform for composition-dependent first-principles investigations. Previous studies have demonstrated that Pb/Sn substitution can effectively tune the band gap and improve the photovoltaic performance of halide perovskites [22–26]. Recent first-principles studies have also demonstrated that compositional modification in halide perovskites can effectively tailor their electronic, optical, and related functional properties, highlighting the importance of theoretical investigations for understanding structure–property relationships in these materials. [27]

Despite the remarkable progress achieved in mixed Pb/Sn halide perovskites, several fundamental challenges remain unresolved, including long-term stability, defect-mediated degradation, and the accurate understanding of their composition-dependent physical properties. The incorporation of Sn into Pb-based perovskites provides an effective strategy for band-gap engineering and extending the light absorption range; however, it also introduces additional challenges associated with Sn^{2+} oxidation, defect formation, ion migration, and material instability [28–30]. Recent studies have highlighted the critical role of defects and compositional instability in governing the degradation mechanisms and limiting the practical application of mixed Pb/Sn halide perovskites [29,30].

Furthermore, the electronic properties of halide perovskites containing heavy elements such as Pb are strongly influenced by relativistic effects, particularly spin–orbit coupling (SOC), which can significantly modify the electronic band structure and optical transition characteristics [28,31]. Therefore, careful consideration of these effects is essential for an accurate interpretation of the electronic properties of lead-based perovskite materials. In addition, excitonic effects and carrier–phonon interactions contribute to the optoelectronic response of halide perovskites and influence their optical behavior [32].

Consequently, establishing a comprehensive relationship between chemical composition, structural configuration, electronic structure, and optical properties remains essential for the rational design of stable and efficient Pb–Sn halide perovskite materials.

Besides the electronic and optical characteristics, the thermodynamic stability of halide perovskites plays a crucial role in determining their practical applicability in photovoltaic and optoelectronic devices. Thermodynamic parameters such as the bulk modulus, Debye temperature, heat capacity, thermal expansion coefficient, and temperature-dependent unit-cell volume provide valuable insight into lattice

stiffness, thermal resistance, anharmonic behavior, and structural stability under operating conditions. Since photovoltaic devices are commonly exposed to varying temperatures, understanding these thermodynamic properties is essential for evaluating the long-term reliability and thermal durability of mixed Pb–Sn perovskites.

In this study, we investigate the effect of Pb–Sn substitution on the structural, electronic, optical, and thermodynamic properties of $CsPb_{1-x}Sn_xBr_3$ perovskites with compositions $x = 0.25$ and $x = 0.75$ using first-principles density functional theory (DFT). The KTB-mBJ exchange potential was employed to obtain a reliable description of the electronic structure and optical properties, while the quasi-harmonic Debye model was used to evaluate the thermodynamic behavior. The primary objective is to clarify how Sn incorporation influences the composition-dependent evolution of the structural stability, electronic structure, optical response, and thermal characteristics of $CsPb_{1-x}Sn_xBr_3$. The obtained results provide a comprehensive understanding of the interplay between composition, thermodynamic stability, and functional properties, demonstrating the potential of these all-inorganic perovskites for optoelectronic applications.

2. Computational methodology

All first-principles calculations were performed using the WIEN2k code, which is based on the full-potential linearized augmented plane wave (FP-LAPW) method within the framework of density functional theory (DFT) [33–35]. The structural properties of cubic $CsPb_{1-x}Sn_xBr_3$ ($x = 0.25$ and 0.75) were investigated using the Wu–Cohen generalized gradient approximation (WC-GGA). The mixed Pb/Sn compositions were modeled using ordered $2 \times 2 \times 1$ supercell configurations derived from the cubic $CsPbBr_3$ structure with space group Pm-3m. In these models, Pb atoms at the B-site were systematically replaced by Sn atoms to obtain the desired Sn concentrations while maintaining an ordered distribution of the substituted atoms.

The Brillouin zone integration and basis-set parameters were carefully selected to ensure reliable results. The convergence of total energy and electronic properties was verified with respect to the k-point mesh and the plane-wave cutoff parameter. The optimized structures obtained from WC-GGA calculations were subsequently used for the investigation of electronic and optical properties.

Since conventional GGA functionals generally underestimate semiconductor band gaps, the electronic structures and optical properties were calculated using the Tran–Blaha modified Becke–Johnson (TB-mBJ) exchange potential. The TB-mBJ approach provides an improved description of the electronic band structure by correcting the exchange potential and yielding more reliable band-gap values compared with standard GGA methods. The TB-mBJ potential was applied consistently to all investigated compositions in order to analyze the effect of Sn substitution on the electronic and optical properties of $CsPb_{1-x}Sn_xBr_3$.

To investigate the thermodynamic behavior of the investigated compounds, temperature- and pressure-dependent thermodynamic properties were calculated using the Gibbs2 code, which is based on the quasi-harmonic Debye model. This approach enables the prediction of thermodynamic properties under conditions that may be difficult to access experimentally. The energy–volume (E–V) data obtained from the DFT calculations were used as input for the Gibbs2 calculations. Within the quasi-harmonic approximation, the non-equilibrium Gibbs free energy, $G(V;P,T)$ was minimized to determine the equilibrium thermodynamic properties as functions of temperature and pressure. Based on this procedure, the bulk modulus (B), Debye temperature (θ_D), constant-volume heat capacity (C_V), thermal expansion coefficient (α), and unit-cell volume (V) were evaluated.

It should be noted that spin–orbit coupling (SOC) effects were not included in the present calculations. Although SOC can influence the electronic structure of Pb-containing halide perovskites, the objective of this work is to investigate the relative modification of structural, electronic, and optical properties induced by Pb/Sn substitution using a

consistent computational framework. Therefore, the same methodology was applied to all compositions, allowing a comparative analysis of the composition-dependent trends.

2.1. Exchange–correlation functionals

The electronic and optical properties were explored using the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) to describe the exchange–correlation interactions of electrons. We employed the modified Becke–Johnson potential (hereafter referred to as KTB-mBJ). The KTB-mBJ provides a more accurate estimation of the band gap compared to other mBJ approaches.

2.2. Computational parameters

The muffin-tin radii (RMT) were uniformly set to 2.5 a.u. for Cs, Pb, Sn, and Br atoms. The plane-wave cutoff parameter $K_{\max}$ was determined using the relation $R_{\text{MT}}K_{\max} = 7.0$, ensuring convergence of the total energy to within 10^{-5} Ry. The self-consistent field (SCF) iterations were considered converged when the charge density difference reached 10^{-3} e. The Brillouin zone was sampled using a Monkhorst–Pack k-point mesh of $10 \times 10 \times 10$ for $x = 0.25$ and $x = 0.75$. This isotropic k-point grid was selected considering the cubic symmetry and comparable lattice parameters of the investigated $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ structures, providing adequate Brillouin-zone sampling while maintaining computational efficiency. The structures were fully relaxed until the forces on each atom were less than 1 mRy/a.u.

The main computational parameters adopted in the present FP-LAPW calculations are summarized in Table 1. The selected values ensured well-converged total energies and reliable structural, electronic, and optical properties for the investigated $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ compositions.

2.3. KTB-mBJ exchange potential formulation

The electronic and optical properties were calculated using the Tran–Blaha modified Becke–Johnson (TB-mBJ) exchange potential within the framework of density functional theory. The TB-mBJ potential was selected because conventional GGA functionals, including WC-GGA, generally underestimate the band gap of semiconductor materials due to the limitations of exchange–correlation approximations. This approach provides a better description of the electronic band structure and optical response of semiconducting systems, particularly for materials containing heavy elements such as Pb.

The KTB-mBJ exchange potential is given by [36,37]:

$$V_{\infty,\sigma}^{\text{mBJ}}(r) = c V_{\infty,\sigma}^{\text{BR}}(r) + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{2t_{\sigma}(r)}{\rho_{\sigma}(r)}} \quad (1)$$

Where:

$V_{\infty,\sigma}^{\text{mBJ}}(r)$: mBJ exchange potential for spin σ

Table 1

Summary of the computational parameters used in the present DFT calculations.

Value	Computational parameter
WC-GGA	Exchange–correlation functional (geometry optimization)
KTB-mBJ	Electronic/optical potential/Thermodynamic
a.u. (Cs, Pb, Sn, Br) 2.5	Muffin-tin radii (RMT)
RMTKMAX = 7.0	Plane-wave cutoff
$10 \times 10 \times 10$ (Monkhorst–Pack)	k-point mesh
Ry 10^{-5}	Total energy convergence
e 10^{-3}	Charge convergence (SCF)
1 mRy/a.u	Force convergence
Cubic	Crystal symmetry
Ordered $2 \times 2 \times 1$	Supercell

$V_{\infty,\sigma}^{\text{BR}}(r)$: Becke – Roussel potential

$\rho_{\sigma}(r)$: Spin – dependent electron density

$t_{\sigma}(r)$: Kinetic energy density for spin σ

In the present work, the TB-mBJ potential was applied after structural optimization performed using the WC-GGA approximation to obtain improved electronic band gaps, density of states, and optical properties of the investigated $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ compositions.

3. Results

3.1. Structural properties

The crystal structures of $\text{CsPb}_{0.75}\text{Sn}_{0.25}\text{Br}_3$, and $\text{CsPb}_{0.25}\text{Sn}_{0.75}\text{Br}_3$ adopt a cubic, corresponding to the $\text{Pm}\bar{3}\text{m}$ space group, with one formula unit ($\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$) per unit cell. Fig. 1 illustrates the three-dimensional arrangement of the cubic unit cell [38].

For the intermediate compositions ($x = 0.25$ and 0.75), an ordered supercell model was constructed by explicitly substituting Pb atoms with Sn at the B-sites in a periodic arrangement. This leads to an alternating distribution of $[\text{PbBr}_6]$ and $[\text{SnBr}_6]$ octahedra within the supercell. The resulting structure represents an idealized ordered approximation of the alloy, which was adopted to ensure structural reproducibility and to enable a consistent comparison with the end-member compounds.

The WC-GGA potential was obtained by analyzing the ground state properties lattice constant (a), bulk modulus (B), and its pressure derivative (B'). While structural optimization was achieved by minimizing the total energy with respect to cell volume [39].

Fig. 2 illustrates the calculated total energy as a function of volume for (a) $\text{CsPb}_{0.75}\text{Sn}_{0.25}\text{Br}_3$, and (b) $\text{CsPb}_{0.25}\text{Sn}_{0.75}\text{Br}_3$. The structural properties of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and $x = 0.75$) were examined using total energy versus volume (E–V) calculations.

All investigated compositions exhibit smooth and well-defined parabolic E–V curves with a single minimum energy point, corresponding to the equilibrium volume of each structure. This behavior indicates that the optimized cubic perovskite configurations are energetically favorable and structurally stable within the framework of the present DFT calculations. A systematic shift of the energy minimum toward lower volumes is observed with increasing Sn concentration, revealing a gradual lattice contraction. This trend can be attributed to the smaller ionic radius of Sn^{2+} compared with Pb^{2+} , resulting in a reduction of the lattice parameters when Sn atoms substitute Pb atoms at the B-site. Furthermore, the absence of discontinuities or additional minima in the calculated E–V curves suggests that the investigated compositions maintain the same cubic structural framework without evidence of structural instability within the considered configurations. These results demonstrate that Pb/Sn alloying provides an effective route for tuning the lattice dimensions of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ while maintaining favorable structural stability. It should be noted that a complete assessment of dynamic stability requires phonon dispersion calculations, which are beyond the scope of the present study.

The calculated structural parameters of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75) compared with previously reported theoretical values for cubic CsPbBr_3 through the lattice constant (a), bulk modulus (B), its pressure derivative (B'), and the equilibrium total energy (E_0), are summarized in Table 2.

It is clearly observed that the lattice constant decreases from 5.8394 Å for $x = 0.25$ –5.7881 Å for $x = 0.75$. This reduction can be attributed to the smaller ionic radius of Sn compared with Pb, resulting in a slight contraction of the crystal lattice as the Sn concentration increases. In contrast, the bulk modulus exhibits only a slight increase from 21.7395 GPa to 22.1535 GPa, indicating that Pb/Sn substitution has only a minor effect on the mechanical stiffness of the cubic lattice. Furthermore, the calculated lattice constants are in good agreement with previously reported theoretical values for cubic CsPbBr_3 , supporting the reliability of the adopted computational approach.

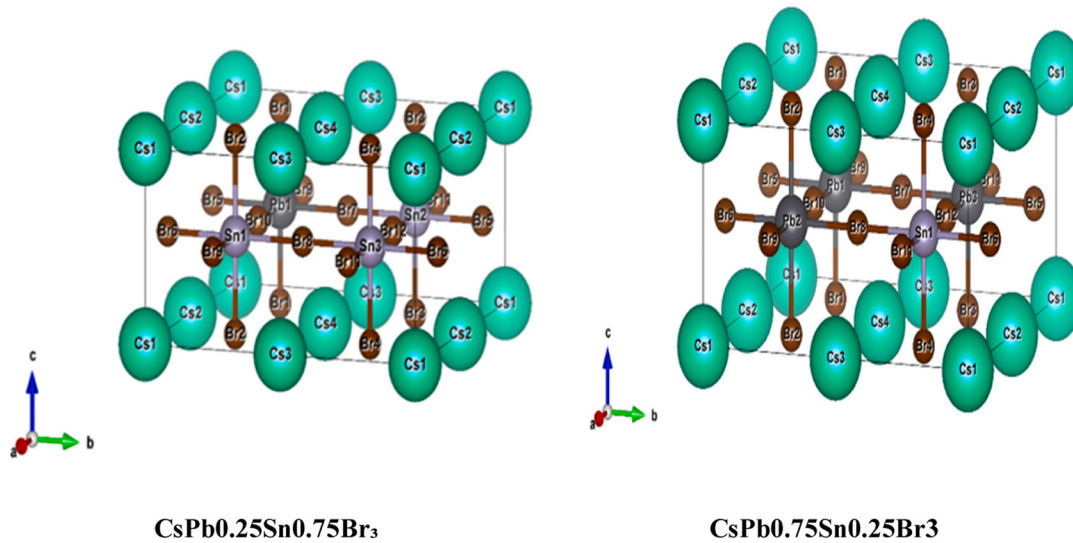


Fig. 1. Cristal structure of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$, with $x = 0.25$ and 0.75 .

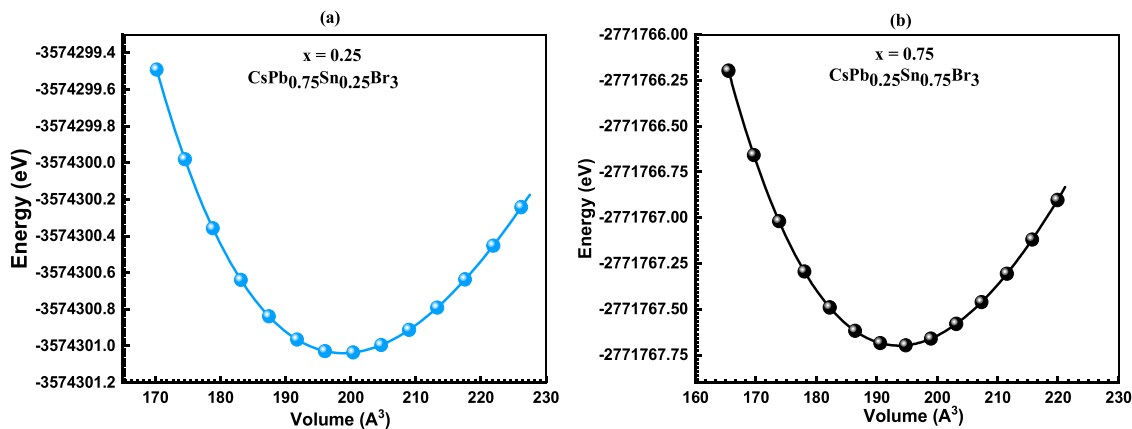


Fig. 2. Calculated total energy versus volume of (a) $\text{CsPb}_{0.75}\text{Sn}_{0.25}\text{Br}_3$ and (b) $\text{CsPb}_{0.25}\text{Sn}_{0.75}\text{Br}_3$.

Table 2

Calculated structural parameters of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75) compared with previously reported theoretical values for cubic CsPbBr_3 .

$\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$	Study	a (Å)	B (GPa)	B'	E_0 (Ry)
x = 0.25	Present study	5.8394	21.7395	4.98449	-262706.0713489
x = 0.75	Present study	5.7881	22.1535	4.1514	-203721.005817
CsPbBr_3	Other study	5.847	20.7379	4.881	-
		[40]	[40]	[40]	-
		5.84	23.5 [41]	5.0 [41]	-

Table 3

Calculated of tolerance factor (t) for cubic $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75).

Composition	Average B-site radius (Å)	Tolerance factor
$\text{CsPb}_{0.75}\text{Sn}_{0.25}\text{Br}_3$	1.1875	0.863
$\text{CsPb}_{0.25}\text{Sn}_{0.75}\text{Br}_3$	1.1825	0.864

Furthermore, the pressure derivative of the bulk modulus (B') decreases from 4.98449 to 4.1514, which may reflect a change in the bonding characteristics and compressibility behavior under pressure.

3.2. Tolerance factor calculation

To further assess the geometrical stability of the cubic $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ structures, the Goldschmidt tolerance factor (t) was calculated. For mixed Pb/Sn compositions, the average ionic radius of the B-site cation was estimated using

$$r_B = (1-x)r_{\text{Pb}^{2+}} + xr_{\text{Sn}^{2+}} \quad (2)$$

The calculated tolerance factors are 0.863 and 0.864 for $\text{CsPb}_{0.75}\text{Sn}_{0.25}\text{Br}_3$ and $\text{CsPb}_{0.25}\text{Sn}_{0.75}\text{Br}_3$, respectively. These values indicate that both investigated compositions are located within the stability range of the perovskite structure, suggesting a favorable geometric arrangement of the Cs-(Pb/Sn)-Br framework. The slight variation in the tolerance factor with increasing Sn content is attributed to the small difference between the ionic radii of Pb^{2+} and Sn^{2+} .

The obtained tolerance factors indicate a geometrically favorable cubic perovskite framework for the investigated compositions.

3.3. Composition-dependent electronic structure

3.3.1. Electronic band structure

Fig. 3 demonstrates the electronic band structures of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75), calculated using the KTB-mBJ exchange potential along the high-symmetry k-path $\Gamma-X-M-\Gamma-R-X$ of the cubic Brillouin zone. The calculated band structures reveal the influence of Pb/Sn

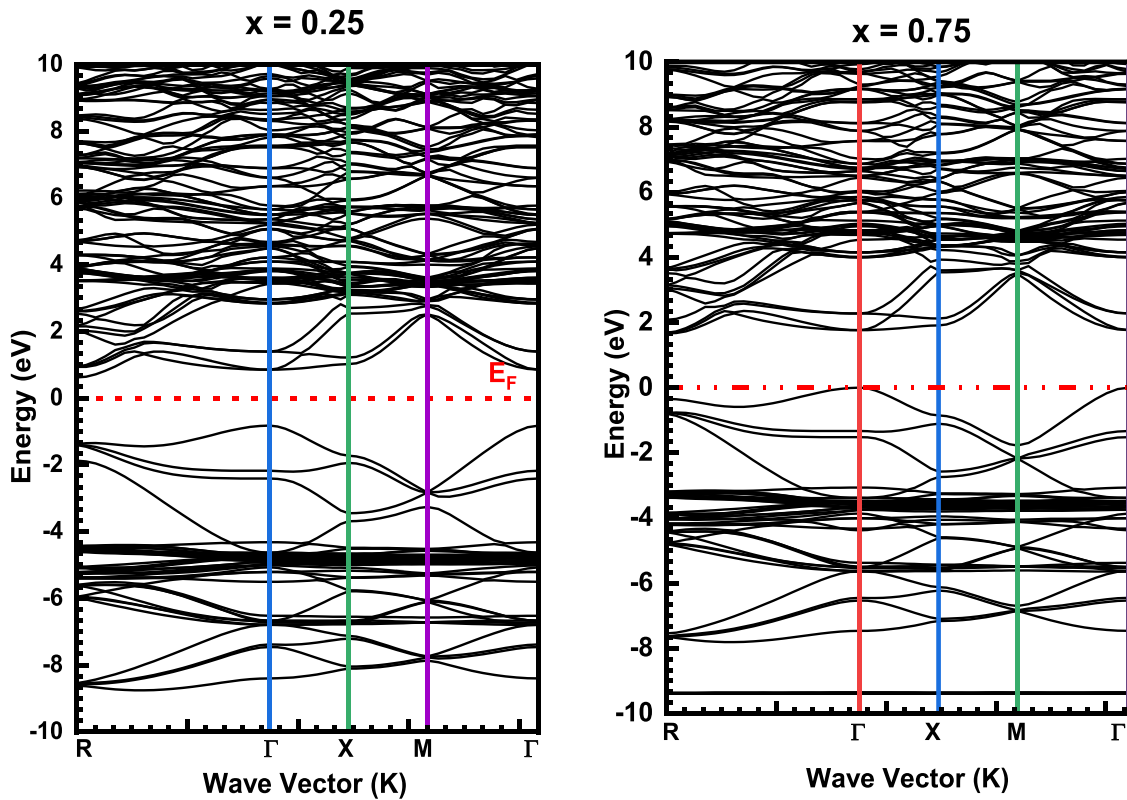


Fig. 3. Calculated band structures of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75) using the KTB-mBJ potential.

substitution on the electronic properties of the investigated compositions. For both compositions, the valence-band maximum (VBM) and the conduction-band minimum (CBM) are located at the R high-symmetry point, confirming the preservation of a direct band-gap character. Previous theoretical studies have reported direct band gaps at different high-symmetry points depending on the computational methodology, exchange–correlation functional, and structural model employed. For example, Ghaithan et al. [42] reported a direct band gap at the Γ point for cubic CsPbBr_3 using FP-LAPW calculations with the mBJ potential, whereas Murtaza et al. [41] reported a direct band gap at the R point. These differences highlight the sensitivity of the band-edge positions to the adopted computational approach. Therefore, the present results are consistent with the direct-band-gap nature generally reported for cubic halide perovskites while demonstrating the influence of Pb/Sn substitution on the electronic structure of the investigated intermediate compositions. The Fermi level lies within the band gap for both investigated compositions, confirming their semiconducting nature. The PDOS analysis shows that the valence-band maximum is mainly dominated by Br–4p states with a minor contribution from Pb/Sn-s orbitals, whereas the conduction-band minimum is primarily composed of Pb–6p and Sn–5p states. As shown in Fig. 3, the calculated band-gap values obtained using the KTB-mBJ potential are 1.45 eV for $\text{CsPb}_{0.75}\text{Sn}_{0.25}\text{Br}_3$ and 1.67 eV for $\text{CsPb}_{0.25}\text{Sn}_{0.75}\text{Br}_3$. The slight increase in the band gap with increasing Sn concentration indicates that Pb/Sn substitution modifies the electronic structure while preserving the direct band-gap character of the investigated compounds.

To evaluate the reliability of the calculated electronic structure, the band-gap values obtained in the present work were compared with previously reported theoretical and experimental data for cubic CsPbBr_3 , as summarized in Table 4. The calculated band gaps of the investigated intermediate compositions are in reasonable agreement with the reported values, with the observed differences being attributable to the partial Pb/Sn substitution, the adopted ordered supercell model, and the use of the KTB-mBJ exchange potential, which is known to provide more

Table 4

Comparison of the calculated band-gap values of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75) with previously reported theoretical and experimental data.

$\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$	Study	E_g (eV)	
		Theoretical	Experimental
$\text{CsPb}_{0.75}\text{Sn}_{0.25}\text{Br}_3$	Present study	1.45	-
$\text{CsPb}_{0.25}\text{Sn}_{0.75}\text{Br}_3$	Present study	1.67	-
CsPbBr_3	Other study	1.6 [41]	2.30 [43]
CsSnBr_3	Other study	1.27 [44]	1.79 [44]

reliable band-gap predictions than conventional GGA functionals.

3.3.2. Density of States (DOS)

The total density of states (TDOS) and partial density of states (PDOS) calculated using the KTB-mBJ potential are presented in Fig. 4. The results show that the valence-band maximum (VBM) is mainly dominated by Br–4p states with minor contributions from Pb-6s and Sn-5s orbitals, whereas the conduction-band minimum (CBM) is primarily composed of Pb–6p and Sn–5p states. The negligible contribution of Cs states near the Fermi level indicates that Cs does not significantly participate in the formation of the band edges. For both investigated compositions, the Fermi level lies within the band gap, confirming their semiconducting nature.

The PDOS analysis further reveals that Pb/Sn substitution modifies the distribution of electronic states near the band edges while preserving the direct-band-gap character of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$. Furthermore, the electronic structure provides a direct interpretation of the calculated optical response. The fundamental optical absorption originates from interband electronic transitions between the occupied Br–4p-derived valence states and the unoccupied Pb–6p/Sn–5p-derived conduction states. Therefore, the composition-dependent evolution of the optical properties is directly correlated with the changes in the electronic states near the band edges induced by Pb/Sn substitution.

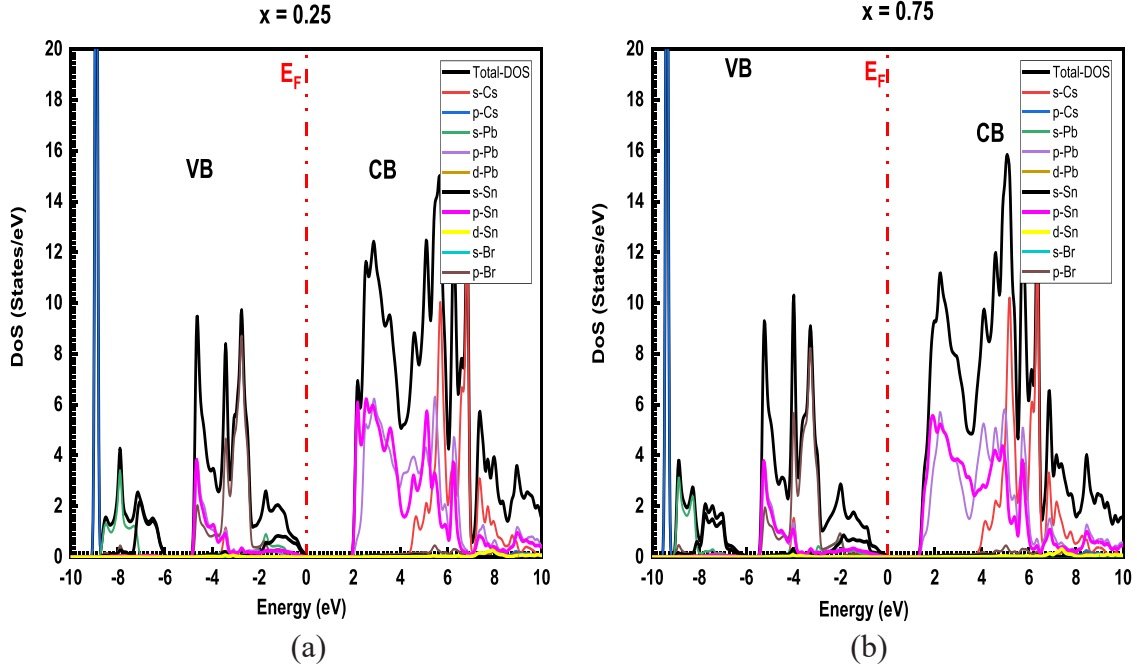


Fig. 4. TDOS and PDOS of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ (a) $x = 0.25$ and (b) $x = 0.75$ calculated using the KTB-mBJ potential.

3.4. Optical properties

The optical properties were evaluated through the complex dielectric function, from which the absorption coefficient, optical conductivity, and refractive index were derived. The analysis focuses on the effect of Sn incorporation on the optical response of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$. Therefore, we investigated these materials' optical absorption, conductivity, reflectivity, as well as their dielectric function, which includes both the real and imaginary parts. The real part, $\epsilon_1(\omega)$, and the imaginary part $\epsilon_2(\omega)$ [45].

Fig. 5(a) illustrates the calculated real part of the dielectric function $\epsilon_1(\omega)$ for $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and $x = 0.75$) under different strain conditions. The static dielectric constant values for the unstrained structure are 3.12 and 3.85 respectively. The increase in the static dielectric constant with increasing Sn content indicates enhanced electronic polarizability, which can be related to the modification of the electronic states near the band edges after Pb/Sn substitution.

The variations of the imaginary part of the dielectric function $\epsilon_2(\omega)$ for $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and $x = 0.75$) under different strain conditions are shown in Fig. 6(b). The imaginary part of the dielectric function $\epsilon_2(\omega)$ has a value of 0 at 0 eV in all structures, indicating no energy dissipation in the material. The highest absorption, marked by prominent peaks, occurs at 16.47 eV and 16.39 eV.

The variation of the dielectric response between $\text{CsPb}_{0.75}\text{Sn}_{0.25}\text{Br}_3$ and $\text{CsPb}_{0.25}\text{Sn}_{0.75}\text{Br}_3$ can be attributed to the modification of the electronic states near the band edges caused by Pb/Sn substitution. The changes in the dielectric function are consistent with the calculated band gap evolution, where the increased Sn content leads to a reduced band gap and consequently modifies the interband optical transitions.

It should be noted that the present optical calculations are performed within the independent-particle approximation; therefore, electron-hole interactions and excitonic effects are not explicitly considered. Such effects can modify the absorption onset near the band-gap energy; however, they do not significantly affect the interpretation of the main interband transitions and the composition-dependent trends discussed here. Furthermore, due to the cubic symmetry of the studied $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ structures, the dielectric response is expected to be essentially isotropic, and no significant optical anisotropy is anticipated.

The Fig. 6 shows the refractive index $n(\omega)$ and extinction coefficients

$k(\omega)$. The spectrum of $n(\omega)$ closely resembles the spectrum of $\epsilon_1(\omega)$. $k(\omega)$ Represents the imaginary extinction coefficient. While $n(\omega)$ corresponds to the real component of the refractive index., as given by [46]:

$$n(\omega) = \frac{1}{\sqrt{2}} \left[\left\{ \epsilon_1(\omega)^2 + \epsilon_2(\omega)^2 \right\}^{1/2} + \epsilon_1(\omega) \right]^{1/2} \quad (3)$$

$$k(\omega) = \frac{1}{\sqrt{2}} \left[\left\{ \epsilon_1(\omega)^2 + \epsilon_2(\omega)^2 \right\}^{1/2} - \epsilon_1(\omega) \right]^{1/2} \quad (4)$$

The calculated refractive index follows the behavior of the real part of the dielectric function. The variation between $x = 0.25$ and $x = 0.75$ reflects the modification of electronic polarizability induced by Pb/Sn substitution. A higher value of $n(\omega)$ indicates stronger interaction between the incident photons and the electronic structure of the material, leading to greater bending of light at the interface.

On the other hand, the imaginary part $k(\omega)$, known as the extinction coefficient, describes the attenuation or damping of light as it propagates through the material. This attenuation mainly arises from absorption processes, where photons transfer their energy to electrons, promoting them to higher energy states, as well as from scattering mechanisms within the crystal lattice. Consequently, larger values of $k(\omega)$ correspond to stronger optical absorption and reduced transparency. As shown in Fig. 6, the variation of $n(\omega)$ with photon energy reflects the dispersion behavior of the material. In the low-energy region, the refractive index remains relatively high due to weak absorption, whereas it decreases gradually with increasing photon energy. Meanwhile, the extinction coefficient $k(\omega)$ remains nearly zero in the low-energy region, indicating negligible absorption below the band gap energy. At higher photon energies, $k(\omega)$ increases significantly due to interband electronic transitions, leading to stronger absorption in the ultraviolet region.

The reflectivity spectra of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$, and 0.75) show a distinct dependence on photon composition and energy. Fig. 7 presents the calculated reflectivity spectra $R(\omega)$. The strong peaks at higher energies are ascribed to interband electronic transitions, but the low reflectivity in the low-energy range suggests modest optical losses and improved light penetration. The observed reduction in reflectivity intensity upon Sn incorporation arises from alterations in the electronic

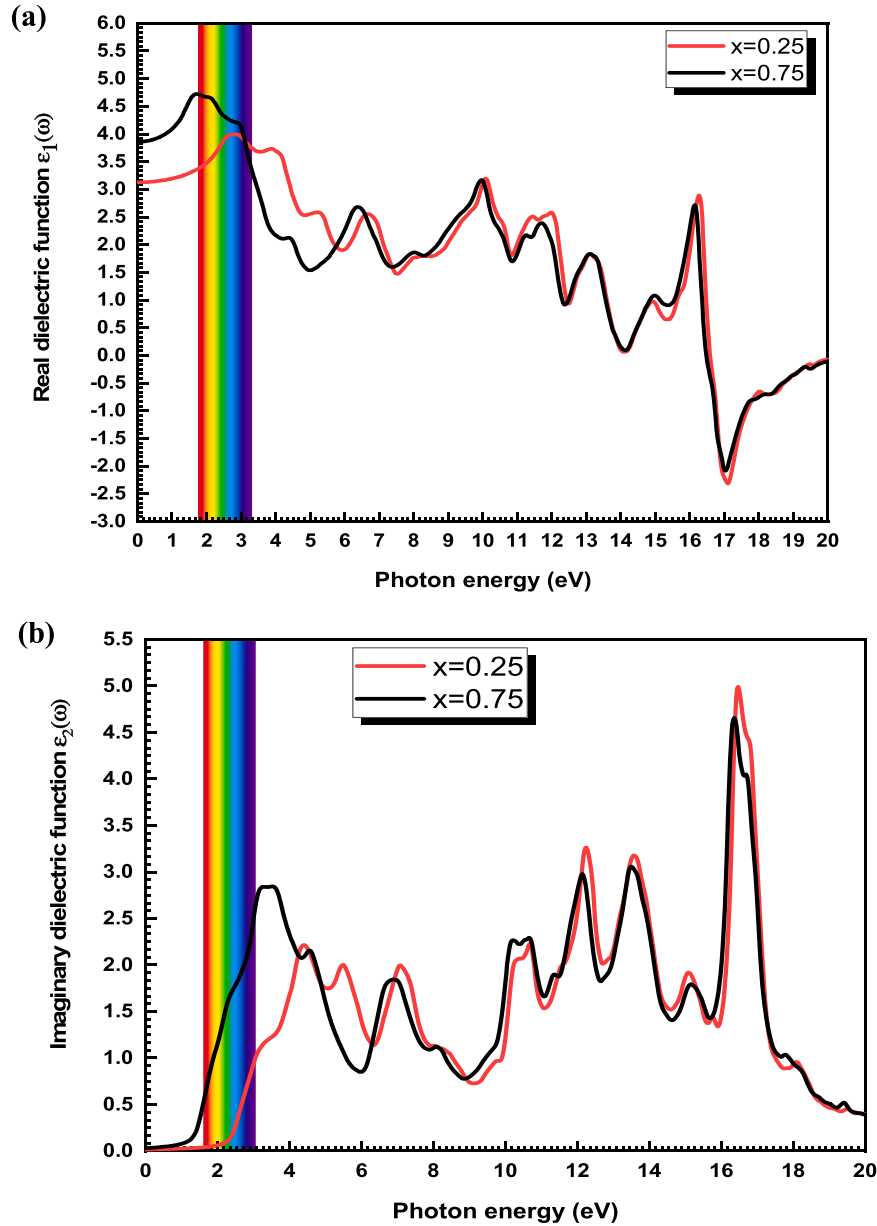


Fig. 5. (a) Real (ϵ_1) and (b) imaginary (ϵ_2) parts of the dielectric function of CsPb_{1-x}Sn_xBr₃ as a function of photon energy, computed using the KTB-mBJ potential.

structure, in good agreement with the evolution of the refractive index and extinction coefficient. The real and imaginary parts of the refractive indices are then used in the following equation to evaluate the reflectivity at normal incidence [47]:

$$R(\omega) = \left| \frac{\tilde{n} - 1}{\tilde{n} + 1} \right|^2 = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \quad (5)$$

Similarly, the absorption coefficient $\alpha(\omega)$ and frequency-dependent optical conductivity $\sigma(\omega)$ are calculated using the following relations:

$$\alpha(\omega) = \frac{4\pi k(\omega)}{\lambda} \quad (6)$$

$$\sigma(\omega) = \frac{2W_{cv}\hbar\omega}{E_0^2} \quad (7)$$

Where

W_{cv} : is transition probability per unit time

Fig. 8 shows the variation of the absorption of coefficient $\alpha(\omega)$ and

optical conductivity $\sigma(\omega)$ as a function of photon energy, at low photon energies, both spectra exhibit weak responses, followed by a sharp increase beyond the optical band gap, indicating the onset of allowed interband electronic transitions. All compositions display high absorption coefficients on the order of 10^4 cm^{-1} in the visible and ultraviolet regions, which is highly favorable for efficient light harvesting in photovoltaic devices. The similar absorption behavior of both compositions indicates that partial Pb/Sn substitution preserves the strong optical activity of the cubic phase. The calculated band gaps increase slightly from 1.45 eV for CsPb_{0.75}Sn_{0.25}Br₃ to 1.67 eV for CsPb_{0.25}Sn_{0.75}Br₃, reflecting the composition-dependent modification of the electronic structure. This trend is consistent with the PDOS analysis, which shows that the valence-band maximum is mainly composed of Br-4p states, whereas the conduction-band minimum is dominated by Pb-6p and Sn-5p states. Consequently, the optical absorption originates from interband transitions between these occupied and unoccupied electronic states. Despite the slight increase in the band gap, both compositions maintain high absorption coefficients over a broad photon-energy range, demonstrating that Pb/Sn substitution effectively tunes the optical

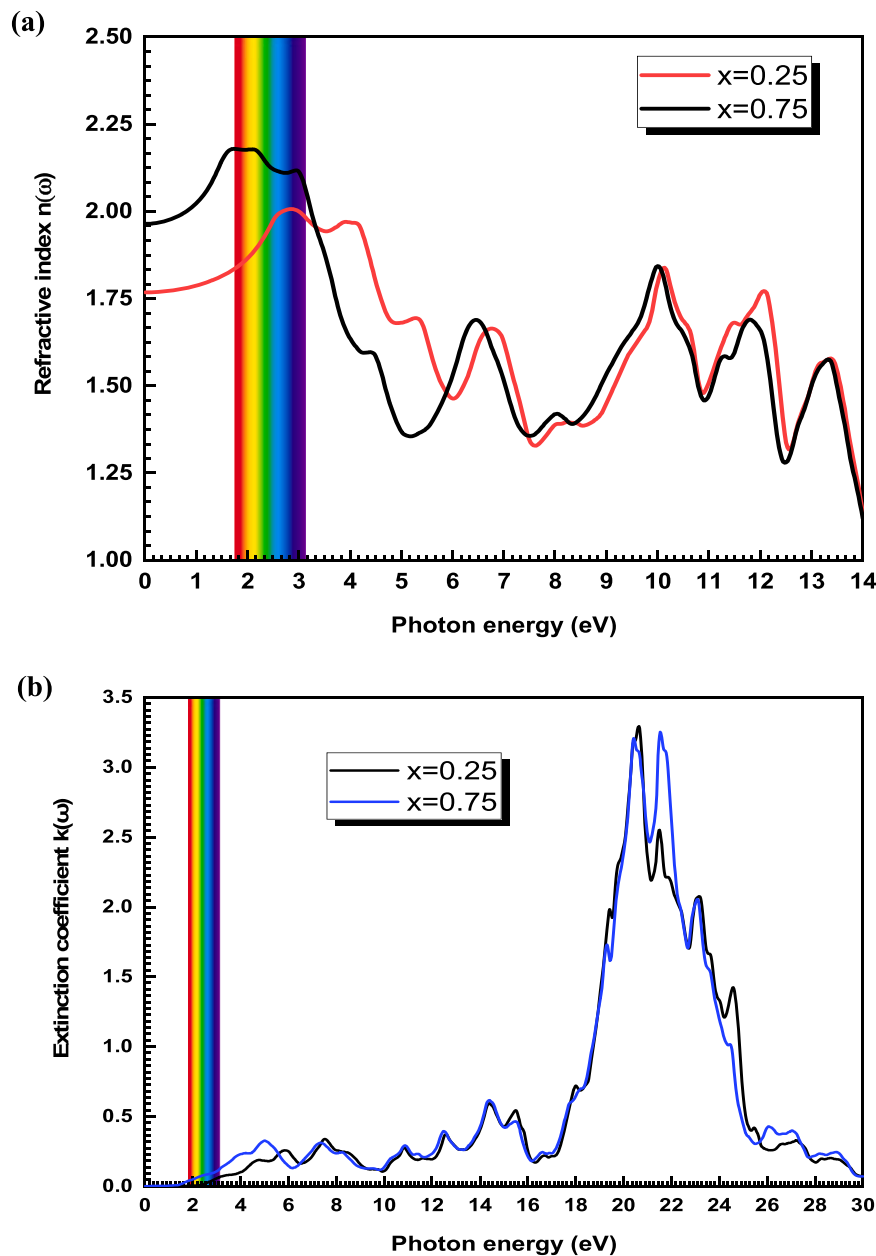


Fig. 6. (a) Photon-energy-dependent refractive index (n) and (b) extinction coefficient (k) of CsPb_{1-x}Sn_xBr₃ ($x = 0.25$, and 0.75) derived from calculations using the KTB-mBJ potential.

response while preserving the favorable optical characteristics of the cubic perovskite structure.

The optical conductivity spectra closely follow the behavior of the absorption coefficient, confirming that photon-induced interband transitions dominate the optical response. These results indicate that controlled Pb/Sn substitution provides an effective approach for tuning the electronic structure and optical response of CsPb_{1-x}Sn_xBr₃, highlighting its potential for optoelectronic applications. The optical conductivity can be further interpreted based on the calculated electronic structure. According to the PDOS analysis, the valence-band maximum is mainly associated with Br-4p states, whereas the conduction-band minimum is dominated by Pb-6p and Sn-5p states. Therefore, the observed conductivity features originate from interband transitions between these occupied and unoccupied electronic states. The similarity of the optical conductivity spectra for both compositions indicates that Pb/Sn substitution modifies the electronic states near the band edges while preserving the characteristic optical response of the cubic perovskite

structure.

3.5. Thermodynamic properties

The thermodynamic properties of CsPb_{1-x}Sn_xBr₃ were calculated using the Gibbs2 algorithm as detailed in the reference [48]. This code is based on Debye's quasiharmonic methodology [49], where by thermodynamic preferences are obtained by minimizing the non-equilibrium Gibbs free energy $G(V;P,T)$ as expressed in the following Eq. (8) [50]:

$$G^*(V,P,T) = E(V) + PV + F_{vib}(V;T) \quad (8)$$

Where $E(V)$ represents the internal energy, P denotes the pressure, V signifies the unit cell volume, and F_{vib} refers to the vibrational Helmholtz free energy at a certain temperature (T), this energy is expressed by the following equation:

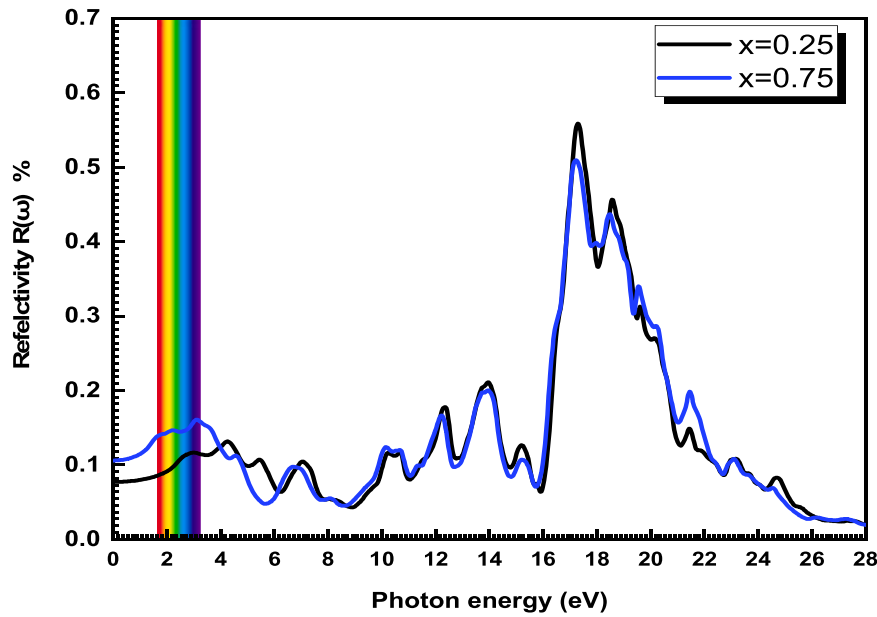


Fig. 7. Calculated optical reflectivity spectra $R(\omega)$ of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ as a function of photon energy based on the KTB-mBJ potential.

$$F_{\text{vib}}(V; T) = nk_B T \left[\frac{9\theta_D}{8T} + 3\ln(1 - e^{-\theta_D/T}) D(\theta_D/T) \right] \quad (9)$$

n , θ_D and $D(\theta_D/T)$ depicts the number of atoms, Debye's temperature and Debye's integral respectively. θ_D is expressed by Eq. (10) [51]:

$$\theta_D = \frac{\hbar}{k} [6\pi^2 V^{1/2} n]^{1/3} f(\sigma) \sqrt{\frac{B_s}{M}} \quad (10)$$

M represents the molecular mass of the unit cell, whereas B_s denotes the adiabatic bulk modulus, which approximates the static bulk modulus ($B_s \cong B(V) = V \frac{d^2 E(V)}{dV^2}$). Consequently, the Gibbs free energy $G^*(V; P, T)$ may be minimized with respect to volume V , yielding Eq. (11):

$$\left[\frac{\partial G^*(V, P, T)}{\partial V} \right]_{P, T} = 0 \quad (11)$$

Thermodynamic equation of state may be derived by solving the preceding Eq. (15). To get the heat capacity (C_V), isothermal bulk modulus (B_T), entropy (S), and thermal expansion coefficient (α), we use the following equations:

$$C_V = 3nk \left[4D\left(\frac{\theta_D}{T}\right) - \frac{3\theta_D/T}{e^{\theta_D/T} - 1} \right] \quad (12)$$

$$S = nk \left[4D\left(\frac{\theta_D}{T}\right) - 3\ln(1 - e^{-\theta_D/T}) \right] \quad (13)$$

$$B(P, V) = V \left(\frac{d^2 G^*(P, V)}{dV^2} \right) \quad (14)$$

$$\alpha = \frac{\gamma C_V}{B_T V} \quad (15)$$

γ is the Grüneisen parameter ($\gamma = -\frac{d \ln \theta(V)}{d \ln V}$)

The temperature dependence of the thermodynamic properties of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ alloys was investigated within the quasi-harmonic Debye approximation over the temperature range of 0–1000 K.

As shown in Fig. 9, the bulk modulus decreases almost linearly with increasing temperature for all Sn concentrations. This behavior originates from thermal expansion, which increases the average interatomic distances and weakens the interatomic bonding strength. Consequently, the resistance of the material to compression decreases at elevated

temperatures.

The variation of the bulk modulus (B) with temperature for $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ at $x = 0.25$ and $x = 0.75$ is shown in Fig. 9; The bulk modulus values reveal a straight downward pattern when temperature climbs from 0 K to 1000 K during the study period (0–1000 K).

For both compositions, the bulk modulus decreases almost linearly with increasing temperature due to enhanced lattice vibrations and thermal expansion, which increase the average interatomic distances and consequently weaken the interatomic bonding strength. As a result, the resistance of the material to compression gradually decreases at elevated temperatures.

The bulk modulus decreases from approximately 21.513 GPa to 13.071 GPa for $x = 0.25$ and from 22.006 GPa to 16.285 GPa for $x = 0.75$ as the temperature increases from 0 to 1000 K. Throughout the investigated temperature range, the $x = 0.75$ composition consistently exhibits slightly higher bulk modulus values than the $x = 0.25$ composition, indicating a relatively stiffer lattice and stronger resistance to compression. Furthermore, the slower decrease in the bulk modulus for $x = 0.75$ indicates that this composition retains a higher resistance to volume compression with increasing temperature, suggesting lower sensitivity to thermal effects than the $x = 0.25$ composition.

Fig. 10 illustrates the temperature dependence of the Debye temperature θ_D for $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75). For both compositions, θ_D decreases gradually with increasing temperature, reflecting the softening of the crystal lattice caused by enhanced atomic vibrations and thermal expansion. The Debye temperature decreases from approximately 159.61 K to 118.75 K for $x = 0.25$, and from 167.94 K to 139.76 K for $x = 0.75$ as the temperature increases from 0 to 1000 K. Throughout the investigated temperature range, the $x = 0.75$ composition exhibits consistently higher Debye temperatures than the $x = 0.25$ composition, suggesting stronger interatomic bonding and enhanced lattice stiffness. Furthermore, the slower decrease in the Debye temperature with increasing temperature indicates greater resistance to thermally induced lattice softening and, consequently, improved thermal stability.

Fig. 11 presents the temperature dependence of the constant-volume heat capacity (C_V) for $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75). For both compositions, the heat capacity increases rapidly with increasing temperature at low temperatures, as expected from the progressive thermal excitation of lattice vibrations within the Debye model. The C_V values increase from $0 \text{ J mol}^{-1} \text{ K}^{-1}$ at 0 K to approximately $123.19 \text{ J mol}^{-1} \text{ K}^{-1}$ for $x = 0.25$ and $122.95 \text{ J mol}^{-1} \text{ K}^{-1}$ for $x = 0.75$ at

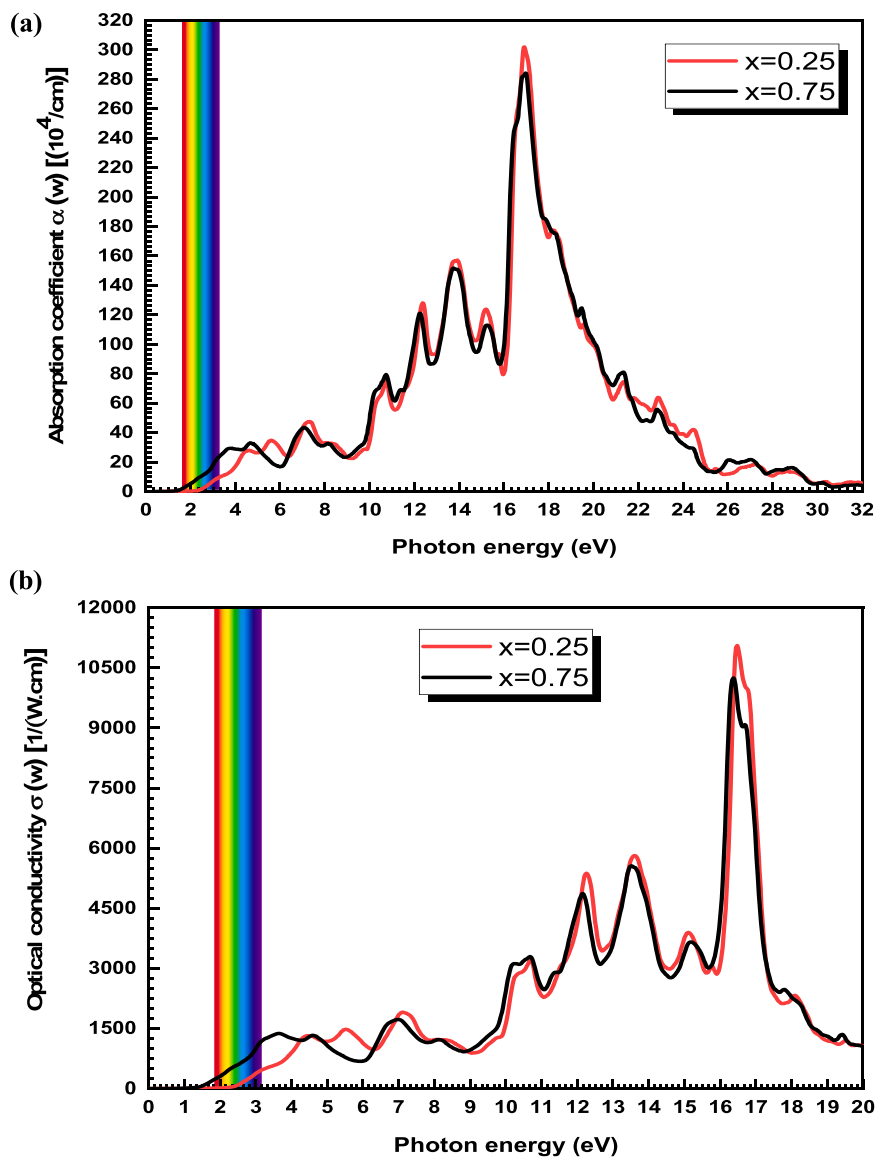


Fig. 8. (a) Photon-energy-dependent optical absorption $\alpha(\omega)$ and (b) conductivity $\sigma(\omega)$ of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$, derived from first-principles calculations using the KTB-mBJ potential.

300 K. At higher temperatures, the rate of increase gradually decreases, and the heat capacity approaches nearly constant values of about $124.63 \text{ J mol}^{-1} \text{ K}^{-1}$ and $124.60 \text{ J mol}^{-1} \text{ K}^{-1}$ at 1000 K for $x = 0.25$ and $x = 0.75$, respectively. These values are close to the classical Dulong–Petit limit, indicating that the heat capacity reaches its high-temperature asymptotic behavior predicted by the Debye model. Furthermore, the nearly overlapping C_v curves indicate that Pb/Sn substitution has only a minor influence on the constant-volume heat capacity, suggesting that the thermal behavior of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ is only weakly affected by the investigated compositions.

Fig. 12 depicts the variation of the thermal expansion coefficient (α) as a function of temperature for $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75). For both compositions, the thermal expansion coefficient increases rapidly at low temperatures and then rises more gradually at higher temperatures. This behavior is consistent with the expected effect of lattice anharmonicity, which becomes increasingly significant as the temperature rises and results in thermal expansion of the crystal lattice.

Throughout the investigated temperature range, the $x = 0.25$ composition exhibits consistently higher thermal expansion coefficients than the $x = 0.75$ composition. At 100 K, α is approximately $10.17 \times 10^{-5} \text{ K}^{-1}$ for $x = 0.25$ and $8.18 \times 10^{-5} \text{ K}^{-1}$ for $x = 0.75$. At

1000 K, these values increase to $16.17 \times 10^{-5} \text{ K}^{-1}$ and $11.29 \times 10^{-5} \text{ K}^{-1}$, respectively. The lower thermal expansion coefficient of the $x = 0.75$ composition indicates a reduced sensitivity to temperature-induced lattice expansion and suggests stronger interatomic interactions, which contribute to improved thermal stability. Therefore, increasing the Sn content from $x = 0.25$ to $x = 0.75$ enhances the resistance of the crystal lattice to thermal expansion.

Fig. 13 represents the temperature dependence of the equilibrium unit-cell volume (V) for $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75). For both compositions, the unit-cell volume increases monotonically with increasing temperature as a consequence of thermal expansion, which enlarges the average interatomic distances within the crystal lattice. The equilibrium volume increases from approximately 1352.74 bohr^3 to 1536.18 bohr^3 for $x = 0.25$, and from 1316.25 bohr^3 to 1449.21 bohr^3 for $x = 0.75$ as the temperature increases from 0 to 1000 K.

the investigated temperature range, $x = 0.25$ composition exhibits consistently larger unit-cell volumes than the $x = 0.75$ composition. This reduction in equilibrium volume with increasing Sn content suggests a more compact crystal lattice and stronger interatomic interactions in the Sn-rich composition. The observed behavior is

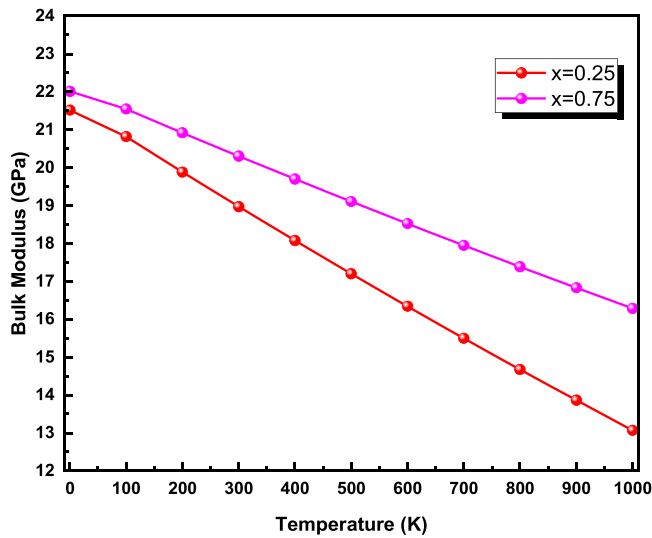


Fig. 9. Temperature dependence of the bulk modulus of cubic $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75) perovskites.

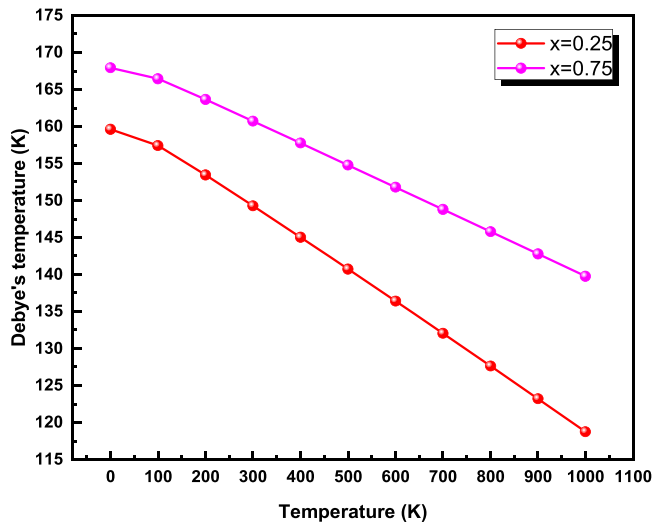


Fig. 10. Temperature dependence of the Debye temperature of cubic $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75) perovskites.

consistent with the higher bulk modulus, higher Debye temperature, and lower thermal expansion coefficient obtained for $x = 0.75$, indicating greater resistance to temperature-induced lattice softening and reduced sensitivity to thermal expansion.

Overall, the calculated thermodynamic properties exhibit physically consistent trends. The decrease in the bulk modulus and Debye temperature with increasing temperature, together with the increase in heat capacity, thermal expansion coefficient, and unit-cell volume, reflects the expected temperature-dependent response of the crystal lattice within the quasi-harmonic Debye model. These results indicate that both investigated compositions exhibit stable thermodynamic behavior over the considered temperature range. Moreover, the Sn-rich composition ($x = 0.75$) maintains a higher bulk modulus and Debye temperature, indicating lower sensitivity to temperature-induced lattice softening than the $x = 0.25$ composition.

4. Conclusion

In this study, the influence of B-site Pb/Sn substitution on the

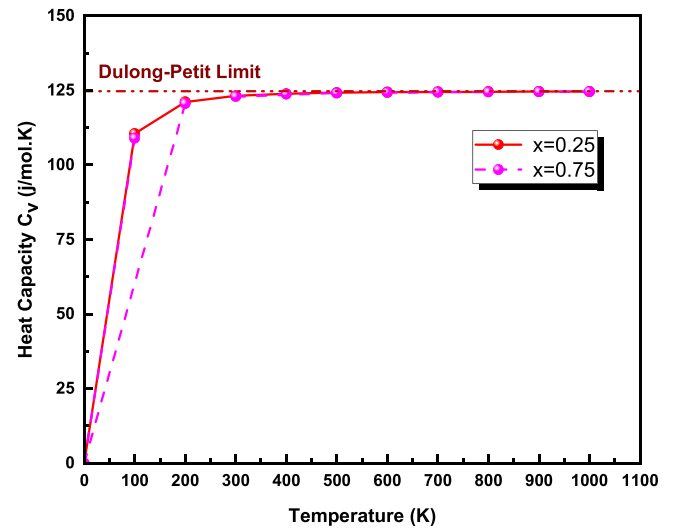


Fig. 11. Temperature dependence of the heat capacity at constant volume (C_v) of cubic $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75) perovskites.

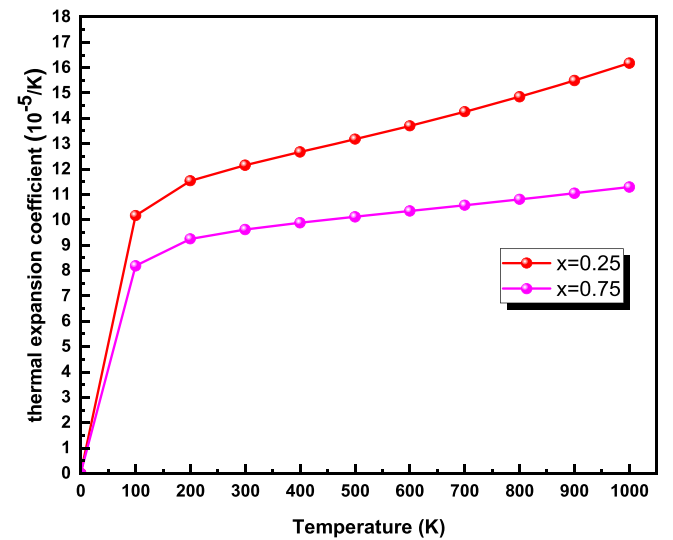


Fig. 12. Temperature dependence of the thermal expansion coefficient (α) of cubic $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75) perovskites.

structural, electronic, and optical properties of cubic $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ perovskites ($x = 0.25$ and 0.75) was systematically investigated using first-principles calculations within the FP-LAPW method. Structural optimization confirmed that both investigated compositions preserve the cubic perovskite structure and remain energetically stable. The electronic structure calculated using the KTB-mBJ exchange potential revealed a direct band gap for both compositions, with values of 1.45 eV for $\text{CsPb}_{0.75}\text{Sn}_{0.25}\text{Br}_3$ and 1.67 eV for $\text{CsPb}_{0.25}\text{Sn}_{0.75}\text{Br}_3$. The partial substitution of Pb by Sn modifies the electronic states near the band edges while preserving the direct-band-gap character. The calculated optical properties, including the dielectric function, absorption coefficient, refractive index, extinction coefficient, optical conductivity, reflectivity, and energy-loss function, exhibit a composition-dependent behavior that originates from interband transitions between Br-4p-derived valence states and Pb-6p/Sn-5p-derived conduction states.*

Furthermore, the thermodynamic properties were investigated within the quasi-harmonic Debye model. All calculated thermodynamic quantities exhibit physically consistent behavior, where the progressive decrease in the bulk modulus and Debye temperature, together with the increase in heat capacity, thermal expansion coefficient, and

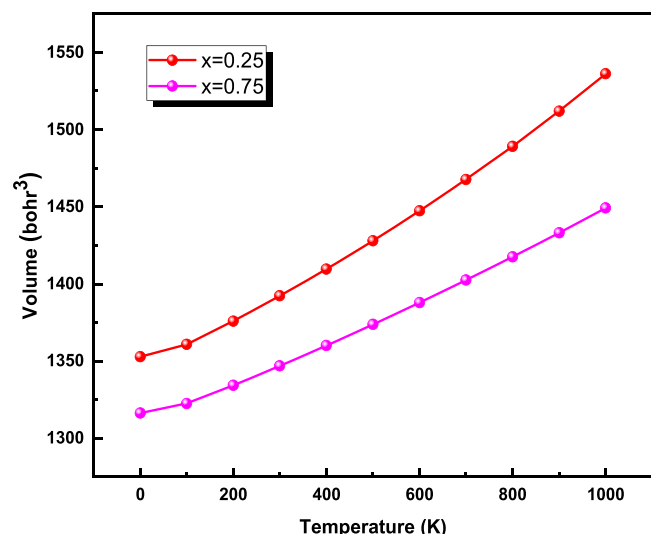


Fig. 13. Temperature dependence of the equilibrium unit-cell volume of cubic $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x = 0.25$ and 0.75) perovskites.

equilibrium unit-cell volume with increasing temperature, reflects the gradual thermal softening of the crystal lattice while maintaining structural stability over the investigated temperature range. Moreover, the Sn-rich composition ($x = 0.75$) exhibits a higher bulk modulus and Debye temperature, accompanied by a lower thermal expansion coefficient and smaller equilibrium volume, indicating enhanced mechanical rigidity and improved thermal stability compared with the $x = 0.25$ composition. These findings suggest that the investigated $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ compounds are promising candidates for optoelectronic and photovoltaic applications operating under varying thermal conditions. Overall, the present results demonstrate that controlled Pb/Sn substitution provides an effective strategy for tailoring the structural, electronic, optical, and thermal properties of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ perovskites, highlighting their potential for future optoelectronic and photovoltaic applications.

CRediT authorship contribution statement

El Hassen Amara: Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Investigation, Formal analysis, Data curation, Conceptualization. **Zeyneb Amara:** Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Nahida Musayeva:** Writing – original draft, Visualization, Validation, Supervision, Methodology, Data curation, Conceptualization. **Hala Mohammadi:** Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the authors used ChatGP and Quillbot to improve the readability and language of the manuscript. After using this tool, the authors carefully reviewed and edited the content and take full responsibility for the content of the publication.

Declaration of Competing Interest

The authors declare that they have no financial or non-financial competing interests.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to thank all those who contributed to this work.

Data Availability Statement

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

References

- [1] W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* 140 (4A) (1965) A1133.
- [2] Z. Li, et al., Stabilizing perovskite structures by tuning tolerance factor: formation of formamidinium and cesium lead iodide solid-state alloys, *Chem. Mater.* 28 (1) (2016) 284–292.
- [3] Q. Lin, et al., Electro-optics of perovskite solar cells, *Nat. Photonics* 9 (2) (2015) 106–112.
- [4] R.A. Jishi, O.B. Ta, A.A. Sharif, Modeling of lead halide perovskites for photovoltaic applications, *J. Phys. Chem. C* 118 (49) (2014) 28344–28349.
- [5] C. Yong-Liang, et al., Progress in perovskite solar cells based on different buffer layer materials, *Acta Phys. Sin.* 69 (13) (2020).
- [6] H. Zhou, et al., Interface engineering of highly efficient perovskite solar cells, *Science* 345 (6196) (2014) 542–546.
- [7] A. Kojima, et al., Organometal halide perovskites as visible-light sensitizers for photovoltaic cells, *J. Am. Chem. Soc.* 131 (17) (2009) 6050–6051.
- [8] H.-S. Kim, et al., Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9, *Sci. Rep.* 2 (1) (2012) 591.
- [9] M.M. Lee, et al., Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites, *Science* 338 (6107) (2012) 643–647.
- [10] S. Trickey, Full-potential, linearized augmented plane wave programs for crystalline systems, *Comput. Phys. Commun.* 59 (1990) 399–415.
- [11] G.K. Madsen, et al., Efficient linearization of the augmented plane-wave method, *Phys. Rev. B* 64 (19) (2001) 195134.
- [12] P. Hohenberg, W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* 136 (3B) (1964) B864.
- [13] Service, R.F., Outlook brightens for plastic solar cells. 2011, American Association for the Advancement of Science.
- [14] F.S. Galasso, properties and preparation of perovskite-type compounds: international series of monographs in solid state physics, in: *Structure*, 5, Elsevier, 2013.
- [15] S. Öz, et al., Zero-dimensional (CH_3NH_3) $_3\text{BiI}_2\text{I}_9$ perovskite for optoelectronic applications, *Sol. Energy Mater. Sol. Cells* 158 (2016) 195–201.
- [16] K.A. Bush, et al., Minimizing current and voltage losses to reach 25% efficient monolithic two-terminal perovskite-silicon tandem solar cells, *ACS Energy Lett.* 3 (9) (2018) 2173–2180.
- [17] A. Miyata, et al., Direct measurement of the exciton binding energy and effective masses for charge carriers in organic-inorganic tri-halide perovskites, *Nat. Phys.* 11 (7) (2015) 582–587.
- [18] D.B. Mitzi, et al., Conducting tin halides with a layered organic-based perovskite structure, *Nature* 369 (6480) (1994) 467–469.
- [19] V. D'Innocenzo, et al., Excitons versus free charges in organo-lead tri-halide perovskites, *Nat. Commun.* 5 (1) (2014) 3586.
- [20] R. Srivastava, Perovskite as light harvester: prospects, efficiency, pitfalls and roadmap, *Nanostruct. Sol. Cells* 314 (2017) 245–276.
- [21] S. Lee, J.S. Cho, D.-W. Kang, Perovskite/polyethylene oxide composites: toward perovskite solar cells without anti-solvent treatment, *Ceram. Int.* 45 (17) (2019) 23399–23405.
- [22] Z. Xing, et al., Photovoltaic performance and stability of fullerene/cerium oxide double electron transport layer superior to single one in pin perovskite solar cells, *J. Power Sources* 389 (2018) 13–19.
- [23] H. Li, et al., Cation-assisted restraint of a wide quantum well and interfacial charge accumulation in two-dimensional perovskites, *ACS Energy Lett.* 3 (8) (2018) 1815–1823.
- [24] Perovskites, O., Theoretical Modeling of Organohalide Perovskites for Photovoltaic Applications.
- [25] X. Liu, et al., Boosting the efficiency of carbon-based planar CsPbBr_3 perovskite solar cells by a modified multistep spin-coating technique and interface engineering, *Nano Energy* 56 (2019) 184–195.
- [26] M. Chen, et al., Highly stable and efficient all-inorganic lead-free perovskite solar cells with native-oxide passivation, *Nat. Commun.* 10 (1) (2019) 16.
- [27] I. Hamideddine, H. Zitouni, N. Tahir, O. El Bounagui, H. Ez-Zahraoui, A DFT study of the electronic structure, optical, and thermoelectric properties of halide perovskite $\text{KGeI}_{3-x}\text{Br}_x$ materials: photovoltaic applications, *Appl. Phys. A* 127 (6) (2021) 443.
- [28] P.K. Kamlesh, S. Sharma, S.K. Bhardwaj, A.S. Verma, Organometallic halide perovskites: futuristic materials for a more efficient and sustainable electronic world, *Hybrid Perovsk. Synth. Prop. Appl.* (2026) 87–140.
- [29] S. Kumar, S.K. Pathak, D. Sharma, P.K. Kamlesh, A.S. Verma, Advancements in antiperovskite structured solids: a comprehensive review, *East. Eur. J. Phys.* (4) (2025) 4–13.

- [30] A. Meena, J.K. Bairwa, S. Kumari, U. Rani, P.K. Kamlesh, A.P. Singh, A.S. Verma, Structural, electronic and optoelectronic characteristics by first principles calculations for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ hybrid perovskite, *Phys. Chem. Solid. State* 26 (1) (2025) 10–22.
- [31] N. Pandit, R. Singh, T.K. Joshi, A. Shukla, P.K. Kamlesh, A. Dubey, A.S. Verma, Investigation of a potential photovoltaic absorber based on first principles spectroscopic screening of chalcogenide perovskites: CaZrX_3 ($\text{X} = \text{S}, \text{Se}$), *J. Comput. Electron.* 24 (1) (2025) 11.
- [32] N. Pandit, A. Dubey, T.K. Joshi, A. Shukla, U. Rani, P.K. Kamlesh, A.S. Verma, Effect of anion (S^{2-} & Se^{2-}) replacement on photovoltaic properties in transition metal (Ba-Barium) chalcogenide perovskites, *Int. J. Mod. Phys. B* 39 (08) (2025) 2550059.
- [33] A.K. Jena, A. Kulkarni, T. Miyasaka, Halide perovskite photovoltaics: background, status, and future prospects, *Chem. Rev.* 119 (5) (2019) 3036–3103.
- [34] Science, A.A.f.t.A.o, Newcomer juices up the race to harness sunlight. *Science* 342 (6165) (2013) 1438–1439.
- [35] Q.A. Akkerman, et al., Solution synthesis approach to colloidal cesium lead halide perovskite nanoplatelets with monolayer-level thickness control, *J. Am. Chem. Soc.* 138 (3) (2016) 1010–1016.
- [36] S. Yakunin, et al., Low-threshold amplified spontaneous emission and lasing from colloidal nanocrystals of caesium lead halide perovskites, *Nat. Commun.* 6 (1) (2015) 8056.
- [37] W. Xiang, et al., Europium-doped CsPbI_2Br for stable and highly efficient inorganic perovskite solar cells, *Joule* 3 (1) (2019) 205–214.
- [38] L. Peedikakkandy, P. Bhargava, Composition dependent optical, structural and photoluminescence characteristics of cesium tin halide perovskites, *RSC Adv.* 6 (24) (2016) 19857–19860.
- [39] Z. Liu, et al., Heavy metal ternary halides for room-temperature x-ray and gamma-ray detection. *Hard X-Ray, Gamma-Ray, and Neutron Detector Physics XV*, SPIE, 2013.
- [40] H.M. Ghaitan, Z.A. Alahmed, S.M. Qaid, A.S. Aldwayyan, Structural, electronic, and optical properties of $\text{CsPb}(\text{Br}_{1-x}\text{Cl}_x)_3$ perovskite: first-principles study with PBE–GGA and mBJ–GGA methods, *Materials* 13 (21) (2020) 4944.
- [41] G.H.U.L.A.M. Murtaza, I. Ahmad, First principle study of the structural and optoelectronic properties of cubic perovskites CsPbM_3 ($\text{M} = \text{Cl}, \text{Br}, \text{I}$), *Phys. B Condensed Matter*. 406 (17) (2011) 3222–3229.
- [42] H.M. Ghaitan, Z.A. Alahmed, S.M. Qaid, M. Hezam, A.S. Aldwayyan, Density functional study of cubic, tetragonal, and orthorhombic CsPbBr_3 perovskite, *ACS Omega* 5 (13) (2020) 7468–7480.
- [43] K. Heidrich, W. Schäfer, M. Schreiber, J. Söchtig, G. Trendel, J. Treusch, H.J. Stolz, Electronic structure, photoemission spectra, and vacuum-ultraviolet optical spectra of CsPbCl_3 and CsPbBr_3 , *Phys. Rev. B* 24 (10) (1981) 5642.
- [44] A. El Badraoui, S. Dahbi, N. Tahiri, O. El Bounagui, H. Ez-Zahraoui, A DFT study of the electronic structure, optical and thermoelectric properties of perovskite CsSnBr_3 compound under strains effect: photovoltaic applications, *Mod. Phys. Lett. B* 38 (07) (2024) 2350237.
- [45] M. Ikram, et al., Solar-triggered engineered 2D-materials for environmental remediation: status and future insights, *Adv. Mater. Interfaces* 10 (11) (2023) 2202172.
- [46] J. Singh, S. Kumar, R. Soni, Synthesis of 3D- MoS_2 nanoflowers with tunable surface area for the application in photocatalysis and SERS based sensing, *J. Alloy. Compd.* 849 (2020) 156502.
- [47] R. Padmavathy, et al., Electronic structure and optical properties of $\text{CsSn}_{1-3-y}\text{Br}_y$ ($y = 0, 1, 2, 3$) perovskites, *Int. J. Mod. Phys. B* 33 (04) (2019) 1950003.
- [48] A. Otero-De-La-Roza, D. Abbasi-Pérez, V. Luana, Gibbs2: a new version of the quasiharmonic model code. II. Models for solid-state thermodynamics, features and implementation, *Comput. Phys. Commun.* 182 (10) (2011) 2232–2248.
- [49] P. Debye, Zur theorie der spezifischen wärmen, *Ann. der Phys.* 344 (14) (1912) 789–839.
- [50] M.A. Blanco, E. Francisco, V.G.I.B.B.S. Luana, GIBBS: isothermal-isobaric thermodynamics of solids from energy curves using a quasi-harmonic Debye model, *Comput. Phys. Commun.* 158 (1) (2004) 57–72.
- [51] A.A. Maradudin, Theory of lattice dynamics in the harmonic approximation, *Solid. State Phys. Suppl.* 3 (1971).