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Research Article

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Posted Date: August 18th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10619451/v1>

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Additional Declarations: No competing interests reported.

Toward Next-Generation Optoelectronic Devices: A Study of the Lead-Free Double Perovskite $\text{Cs}_2\text{CuSbCl}_6$

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Abstract

Halide double perovskite (HDPV) $\text{Cs}_2\text{CuSbCl}_6$ nanoparticles were successfully synthesized via a facile precipitation route under acidic conditions. Comprehensive structural characterization of the as-prepared sample by X-ray diffraction (XRD) and infrared (IR) spectroscopy confirmed the formation of a cubic $\text{Cs}_2\text{CuSbCl}_6$ phase with $\text{Fm}\bar{3}\text{m}$ symmetry and an average crystallite size of 29.34 nm. High-resolution transmission electron microscopy (HRTEM) further verified the nanoscale morphology of $\text{Cs}_2\text{CuSbCl}_6$, revealing an average particle size of 31.34 nm. Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability of the HDPV and to derive the associated kinetic and thermodynamic parameters. Diffuse reflectance spectroscopy (DRS) revealed a narrow direct band gap of 1.2 eV coupled with a notably low Urbach energy of 0.22 eV. The normal dispersion of the refractive index was well described by the Cauchy model. Furthermore, the Wemple–DiDomenico and Drude models were applied to determine the dispersion and oscillator energies, static dielectric constant, static refractive index, and free-carrier concentration, revealing strong consistency among the derived optical parameters. Based on the Mulliken electronegativity approach, the conduction band (E_{CB}) and valence band (E_{VB}) potentials of $\text{Cs}_2\text{CuSbCl}_6$ were determined to be +1.25 V and +2.45 V in relation to the Normal Hydrogen Electrode (NHE), respectively. The E_{VB} value exceeds the redox potentials of both $\text{H}_2\text{O}/\text{O}_2$ (+1.23 V) and $\text{OH}^-/\bullet\text{OH}$ (+1.99 V), indicating strong oxidative capability sufficient to drive both direct water oxidation and hydroxyl radical generation. In contrast, the E_{CB} potential of +1.25 V is too positive to support proton reduction to H_2 , since hydrogen evolution requires an E_{CB} more negative than 0 V vs. NHE. These band positions suggest that $\text{Cs}_2\text{CuSbCl}_6$ is better suited for photocatalytic oxidation processes, such as pollutant degradation, than for photocatalytic hydrogen production.

Key words: Halide double perovskite; refractive index; free-carrier concentration; Cauchy model; Mulliken electronegativity; photocatalytic oxidation.

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1. Introduction

Over the past decade, halide double perovskites (HDPVs) have been among the most investigated classes of semiconducting materials, owing to their prospective applications in photovoltaics and optoelectronics. HDPVs are promising candidates to replace the traditional Pb-based halide perovskites (HPVs) [1], [2] in the next generation of lead-free, compositionally tunable, and structurally stable materials. The general formula of these materials is $\text{A}_2\text{BB}'\text{X}_6$, where A is a relatively large monovalent cation, such as methylammonium (MA^+), formamidinium (FA^+), or Cs^+ , while B and B' are a pair of hetero-valent metal cations, usually a monovalent/trivalent combination, and X denotes a halide anion such as Cl^- , Br^- , or I^- [3], [4].

The DPV architecture introduces an additional degree of compositional and structural flexibility through various cation substitutions, enabling exceptional tunability of electronic structure, lattice dynamics, magnetic ordering, and optical characteristics [5], [6]. Meanwhile, the unique optoelectronic properties of lead-based perovskites, together with their low-cost fabrication and remarkable photovoltaic performance, have placed them at the front edge of next-generation solar cell technology [7], [8]. However, the widespread commercialization of Pb-based PVs has encountered several obstacles due to the environmental risks associated with the toxicity of Pb^{2+} ions and their poor stability against air, heat, and moisture [9], [10]. Consequently, these challenges have inspired substantial efforts to develop earth-abundant, environmentally friendly, and chemically stable alternatives [5]. Among the highly recommended candidates, lead-free HDPVs have gained considerable scientific interest due to their better chemical and thermal stability [11]. Thus, the crystal structure of HDPVs exhibits significant resilience to substitutions at the B and B' sites with cations of different valence states, which renders them able to tune light absorption, bandgap energy, and charge carrier mobility [12]. Such structural versatility allows the design of a powerful platform for engineering multifunctional materials with potential applications in photovoltaics, photocatalysis, and spintronics [13]. In particular, chloride-based double perovskites (Cl-DPVs) are typically reported to show superior structural robustness owing to strong metal–halide bonding and lattice rigidity, which suppress phase degradation and hence ensure long-term operational stability [14]. Among numerous Pb^{2+} -free Cl-DPVs, $\text{Cs}_2\text{CuSbCl}_6$ has recently garnered significant research interest because of its remarkable electronic configuration and promising semiconducting properties. Moreover, the octahedral framework involves monovalent Cu^+ and trivalent Sb^{3+} cations, which generate remarkable orbital hybridization that profoundly influences the band structure and optical transitions [15], [16]. The incorporation of Cu-derived electronic states plays a pivotal role in controlling charge transport and, thereby, the light absorption, whereas the stereochemically active lone pair of electrons on antimony (Sb^{3+}) significantly impacts the lattice dynamics and valence band (V.B.) structure [17], [18], [19]. In view of these peculiar features, the present work focuses mainly on the successful synthesis of the lead-free $\text{Cs}_2\text{CuSbCl}_6$, followed by detailed characterization with particular emphasis on its structural, thermal, optical, and electronic properties. A thorough understanding of these characteristics is essential to assess the relevance of the material to future optoelectronic applications, while concurrently contributing to the development of stable, eco-friendly, and compositionally tunable perovskite-based semiconductors.

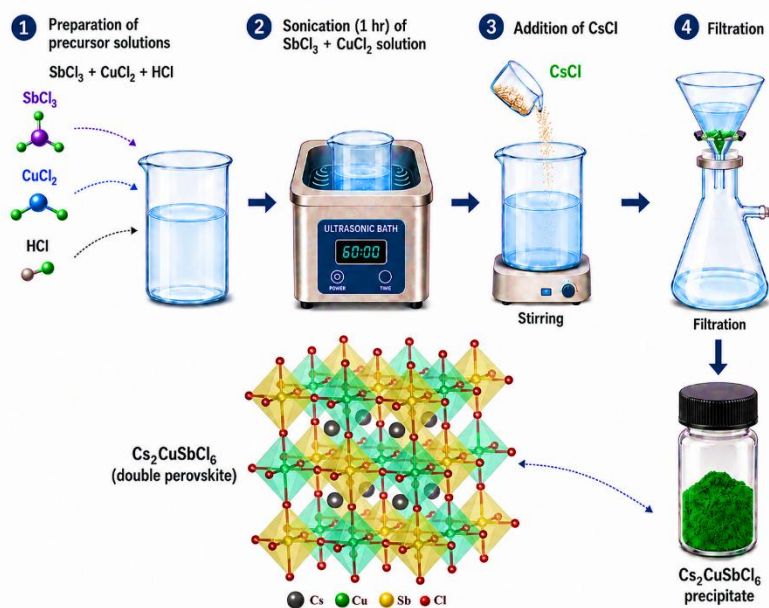
2. Experimental work

2.1 Materials and preparation of $\text{Cs}_2\text{CuSbCl}_6$ nanoparticles (NPs)

Cesium chloride (CsCl), Antimony chloride (SbCl_3), Cupric Chloride (CuCl_2) and Hydrochloric acid (HCl , 37%) were used as precursor materials. Fig.1 shows the preparation procedure of $\text{Cs}_2\text{CuSbCl}_6$ NPs which are performed through precipitation from acidic solution [1]. Firstly, CsCl was dissolved in distilled water under magnetic stirring for 20 min. On the other hand, SbCl_3 and CuCl_2 were dissolved in 10 ml of concentrated HCl separately and then added together to form a mixed solution, which was subsequently sonicated for one hour. The CsCl solution was then gradually added to the $\text{CuCl}_2/\text{SbCl}_3$ mixture, resulting in the immediate formation of a dark green precipitate. The obtained product

was collected by filtration and washed several times with ethanol to remove unreacted species and enhance the phase crystallinity. Finally, the precipitate was dried and formed a very fine $\text{Cs}_2\text{CuSbCl}_6$ powder.

Fig.1. Schematic diagram of preparation procedure of $\text{Cs}_2\text{CuSbCl}_6$ nanoparticles.



2.2 Characterization Techniques

Thermogravimetric (TGA) and differential thermal analyses (DTA) were used to assess the thermal stability of the samples by using a Shimadzu (model DTGA-60) differential thermal gravimetric analyzer and a Shimadzu (model DSC-50) differential scanning calorimeter, respectively. The powder X-ray diffraction (PXRD) pattern of the studied NPs was determined using $\text{Cu-K}\alpha$ radiation ($\lambda = 0.1542$ nm from a Cu X-ray tube, with a line source of 12×0.04 mm², using an X' Pert PRO analytical diffractometer. PXRD analysis was utilized to evaluate the crystallite size of the Cl-DPVs investigated. The molecular structure was characterized by Fourier Transform Infrared (FTIR) Spectroscopy using the IR-Affinity-1 model. The morphological features of the Cl-DPVs were examined by employing High Resolution Transmission Electron Microscopy (HRTEM) using the Tecnai G20 super twin, double-slit model. The histogram of the particle size distribution of the NPs was analyzed using Image-J software. A Jasco V-570 spectrophotometer was used for UV spectroscopy to study the optical properties of the sample under investigation.

3. Results and Discussion

3.1 Structural analyses

3.1.1 Powder X-ray Diffraction (PXRD)

Figure 2 illustrates the PXRD pattern of the as-prepared Cl-DPV $\text{Cs}_2\text{CuSbCl}_6$. The diffractogram reveals a well-defined series of sharp, intense Bragg reflections, spanning a broad 2θ range, confirming the formation of a crystalline phase for Cl-DPV. These results are in good agreement with previously reported Cl-DPVs [2], [3], [4]. In particular, the dominant reflections observed at 2θ : 23.55° , 24° , 29° , and 34° serve as diagnostic fingerprints of a cubic crystal system, consistent with an ordered Cl-DPV framework. Fig.2a shows that $\text{Cs}_2\text{CuSbCl}_6$ adopts a cubic structure with the space group $\text{Fm}\bar{3}\text{m}$, and $Z = 4$. The unit cell parameters are $a = b = c = 10.757 \text{ \AA}$, with a corresponding unit cell volume of $1244.8 \text{ \AA}^3$ [5], [6]. Within the present three-dimensional structure, corner-sharing $[\text{CuCl}_6]^{5-}$ and $[\text{SbCl}_6]^{3-}$ octahedra alternate in a rock-salt ordering, coordinated by six halide ions (Cl^-) at the vertices as shown in Fig. 2b. The Cs^+ cations occupy the twelve-coordinate cub-octahedral voids [7]. The crystallite size (D) of the $\text{Cs}_2\text{CuSbCl}_6$ sample was estimated by applying the Scherrer equation [8], providing an average D of 29.34 nm . The broad diffraction peaks along with the nanoscale size suggest that the as-synthesized $\text{Cs}_2\text{CuSbCl}_6$ possesses a well-developed, highly ordered crystalline structure.

Despite the largely successful synthesis of the Cl-DPVs phase, a minor secondary phase was detected and attributed to an Sb^{3+} -rich $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ trigonal phase, which appeared at $2\theta = 14.4^\circ$ [9]. The formation of this competing phase is well-documented in various HDPV systems [5], [9], [10], [11]. This behavior has been attributed to the tendency of Cu^{2+} to redirect the crystallization process toward the thermodynamically favored trigonal polymorph, which exhibits a lower formation energy [29].

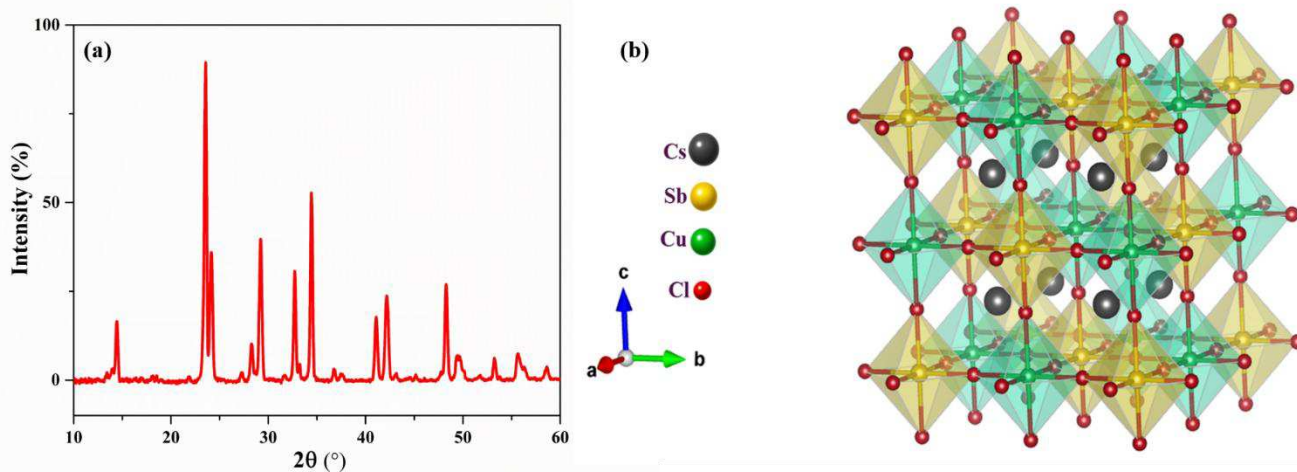


Fig. 2. (a) PXRD diffraction pattern of $\text{Cs}_2\text{CuSbCl}_6$, (b) Crystal structure of $\text{Cs}_2\text{CuSbCl}_6$ Cl-DPV.

To confirm the stability of $\text{Cs}_2\text{CuSbCl}_6$ compounds in cubic phase, we have calculated the values of octahedral factor (μ), the Goldschmidt tolerance factor (τ), and the new tolerance factor (ξ), which are defined as follows[12], [13], [14]:

$$\mu = \frac{r_{\text{Sb}} + r_{\text{Cu}}}{r_{\text{Cl}}} \quad (1)$$

$$\tau = \frac{r_{\text{Cs}} + r_{\text{X}}}{\sqrt{2} \left(\frac{r_{\text{Sb}} + r_{\text{Cu}}}{2} + r_{\text{X}} \right)} \quad (2)$$

$$\xi = \frac{r_{\text{X}}}{r_{\text{B}}} - n_{\text{A}} \left[n_{\text{A}} - \frac{\left(\frac{r_{\text{A}}}{r_{\text{B}}} \right)}{\ln \left(\frac{r_{\text{A}}}{r_{\text{B}}} \right)} \right] \quad (3)$$

Where r_{Cs} (coordination number 12), r_{Sb} , r_{Cu} , and r_{X} (coordination number 6) represent the radius of Cs, Sb, Cu, and Cl atoms, respectively, and n_{A} denotes the oxidation state of Cs. If the values of these factors fall in the range of 0.415 and 0.895 for μ , 0.813 and 1.107 for τ , and below 4.18 for ξ , the Cl-DPV are regarded as stable in cubic symmetry [15], [16], [17], which are in good agreement with the obtained data as presented in Table 1.

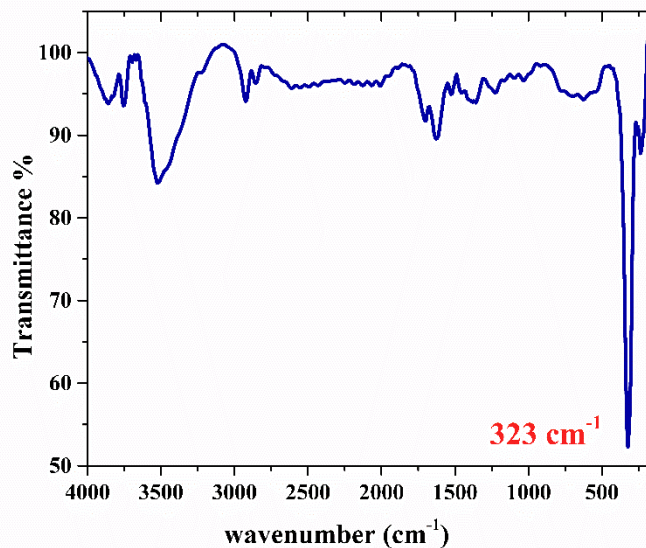
Table 1 Lattice parameters, octahedral factor (μ), the Goldschmidt tolerance factor (τ), and the new tolerance factor (ξ) for various chloride double perovskites.

Samples	$a = b = c$ (Å)	V (Å ³)	μ	τ	ξ	Reference
$\text{Rb}_2\text{AgAsCl}_6$	10.480	1151	0.48	0.93	3.99	[18]
$\text{Cs}_2\text{AgRhCl}_6$	10.087	1026.2	0.5	0.96	3.84	[19]
$\text{Cs}_2\text{CuSbCl}_6$	10.757	1244.8	0.44	0.96	4.09	The present work

3.1.2. FT-IR Spectroscopy

FT-IR spectroscopy in transmittance mode was utilized to verify the structural integrity of $\text{Cs}_2\text{CuSbCl}_6$ Cl-DPVs, as illustrated in Fig. 3 [20], [21]. Based on group theory calculations, four infrared-active modes ($4F_{1u}$) are consistent with $\text{Fm}\bar{3}\text{m}$ cubic perovskite symmetry [20], [21]. In the fingerprint region, the absorption near 590 cm^{-1} is ascribed to metal–halide bending vibrations within the perovskite lattice, while the Sb–Cl and Cu–Cl stretching modes of the $[\text{SbCl}_6]^{2-}$ and $[\text{CuCl}_6]^{5-}$ octahedral units are expected in the far-IR region at 250 cm^{-1} and 323 cm^{-1} , respectively [7], [9], [22]. These bands provide evidence of the formation of the inorganic perovskite framework. The broad absorption band observed in the 3450–3500 cm^{-1} region is assigned to the O–H stretching vibrations of adsorbed H_2O molecules and/or surface hydroxyl groups. The absence of intense peaks in the wavenumber above 1000 cm^{-1} indicates the formation of a pure inorganic phase, with no evidence of contamination or residual precursors [23].

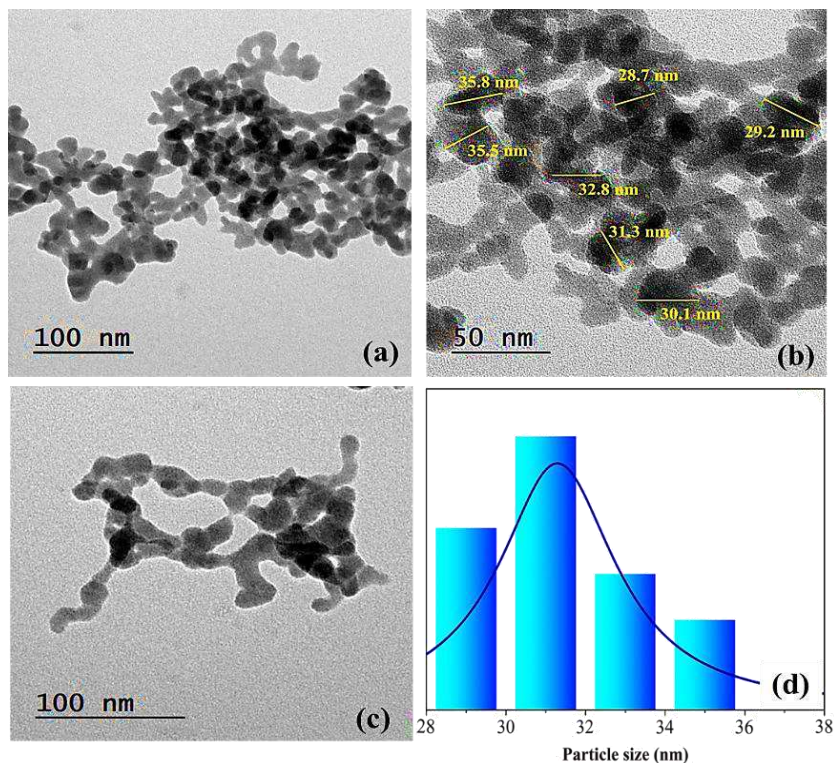
Fig.3. FT-IR spectrum of $\text{Cs}_2\text{CuSbCl}_6$ DPV.



3.1.3 HRTEM

HRTEM is an advanced characterization method that delivers direct structural information at the atomic scale for Cl-DPV. HRTEM micrographs facilitate the evaluation of particle morphology, size distribution, and surface features, which encompass the identification of distinct boundaries and the extent of aggregation. The nanosized nature of $\text{Cs}_2\text{CuSbCl}_6$ was investigated through the HRTEM images as depicted in Fig. 4 (a-d). The $\text{Cs}_2\text{CuSbCl}_6$ NPs display well-defined boundaries and a narrow size distribution, accompanied by minor aggregation.

Fig. 4. (a-c) HRTEM images and (d) Histogram of particle size distribution of $\text{Cs}_2\text{CuSbCl}_6$ NPs.



The particle sizes obtained from HRTEM images are shown in the histogram in Fig. 4d. They are generally fitted with a Gaussian distribution to obtain statistically dependable estimates of the mean particle size, which often resides within the nanometer scale (31.34nm). Such uniformity and well-defined edges are indicative of a controlled synthesis technique.

3.1.4 Thermal analyses

The thermal stability of $\text{Cs}_2\text{SbCuCl}_6$ was evaluated using thermogravimetric analysis (TGA) and differential thermal analysis (DTA), as shown in Fig. 5a, over the temperature range of 300–1200 K. The graph shows a three-step thermal degradation process. It demonstrates a limited weight loss (WL) below 10% up to 1200 K, without rapid degradation of the studied HDPV, confirming its initial stability towards temperature variation [1]. In the first region, the TGA curve reveals that the Cl-DPV remains largely stable up to approximately 580 K, with only a marginal WL of about 2%, which can be attributed to the removal of surface-adsorbed moisture or residual solvent [24]. Beyond this temperature, a significant WL of 6% is observed in the second region, ranging from approximately 580 K to 800 K. This major thermal stage is likely linked to the loss of halides and the decomposition of metal halides [33]. Next, there is a slight WL up to 1200 K, where the residual mass remains stable at around 90%, and that points to the formation of the thermally stable breakdown product of $\text{Cs}_2\text{CuSbCl}_6$. The accompanying DTA curve shows an exothermic peak near 600 K, which agrees well with the significant WL event detected in the TGA plot and can be ascribed to a structural phase transition or the onset of decomposition. At higher temperatures, another broad exothermic to endothermic behavior is observed, with a small anomaly in the range of 1050–1100 K, which may indicate secondary structural rearrangements or partial decomposition of intermediate phases. The TGA-DTA study hence verifies that $\text{Cs}_2\text{CuSbCl}_6$ possesses good thermal stability and can therefore be used for potential applications in optoelectronic devices that function under moderate thermal conditions.

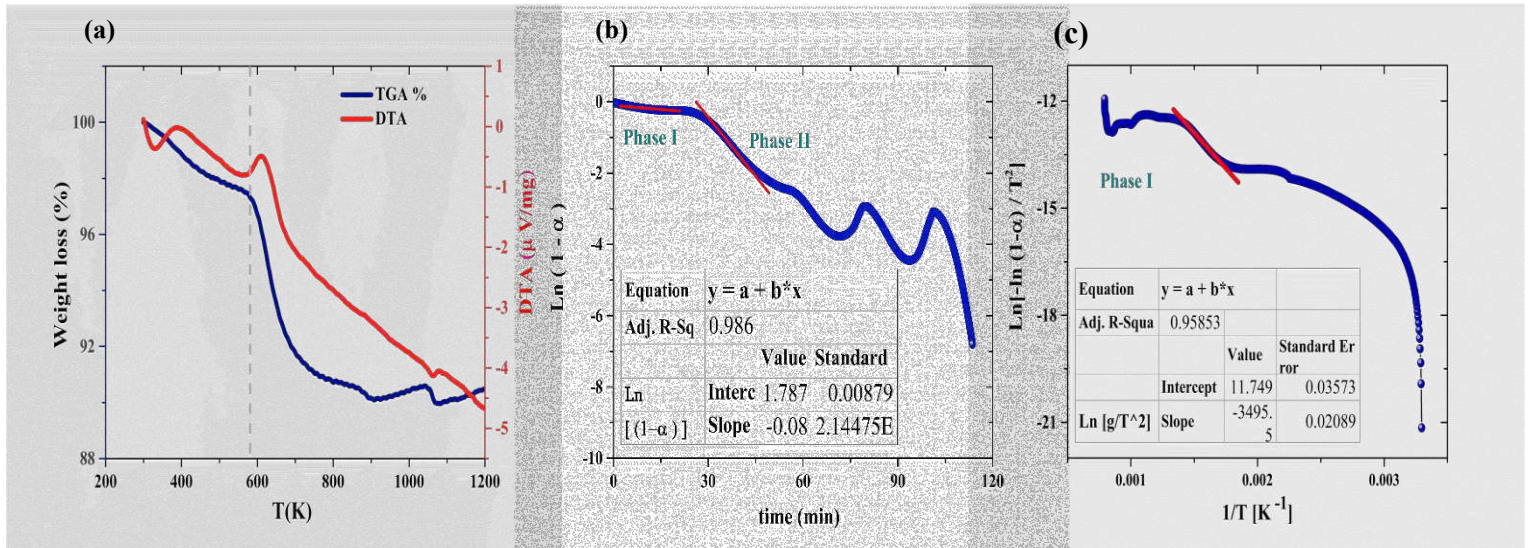


Fig.5. (a) TGA-DTA thermographs of $\text{Cs}_2\text{CuSbCl}_6$ DPV, **(b)** Plot of $\ln(1-\alpha)$ vs. time (min.). **(c)** Graph of $\text{Ln}[-\ln(1-\alpha)/T^2]$ vs. $1/T$ (K^{-1}).

The TGA data were evaluated using the Coats-Redfern fitting model [25], which delineates the decomposition curve into two distinct phases (I, II) at characteristic temperatures of 298 K and 516 K, respectively. Derivation of kinetic and thermodynamic parameters was employed by considering that thermal degradation of the material under investigation follows a pseudo-first Order (PFO) reaction rate equation given by the following rate equation [26]:

$$\frac{d\alpha}{dt} = k(1 - \alpha) \quad (4)$$

This equation is further modified after integration as follows:

$$\ln(1 - \alpha) = -kt \quad (5)$$

The fractional WL (α) is calculated using the upcoming equation: $\alpha = \frac{w_i - w_t}{w_i - w_f}$ (6)

As w_i and w_f refer to the weights of the sample at the beginning and the end of the TGA experiment, whereas w_t is the weight at a specific time. By plotting $\ln(1 - \alpha)$ versus time (Fig. 5b), the rate constant (k) can be estimated from the slope of the linear portion for Phase II. Accordingly, the half-life time ($t_{1/2}$) can be calculated using the equation [27]:

$$t_{1/2} = \frac{\ln 2}{k} \quad (7)$$

Thermodynamic parameters can be calculated by using Coats-Redfern model, which is represented by the following equation [25]:

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT} \quad (8)$$

Where A is assigned to a pre-exponential factor, R stands for the universal gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), while β denotes the linear heating rate. T is the temperature in Kelvin (K), and E_a refers to the activation energy. The values of E_a and A are estimated from the plot of the left-hand side of equation (8) including $\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right]$ versus $1/T$, as demonstrated in Fig. 5c. The thermal decomposition reaction's entropy (ΔS), enthalpy (ΔH), and Gibbs free energy (ΔG) are determined at the maximum decomposition rate ($T_{\max}$), which is derived from the DTG curve for each stage of decomposition, based on the E_a and A values, using the following equations [28], [29]:

$$\Delta H = E_a - RT \quad (9)$$

$$\Delta S = R \ln(Ah/kBT_p) \quad (10)$$

$$\Delta G = \Delta H - T \Delta S \quad (11)$$

where k_B and h represent the Boltzmann ($1.381 \times 10^{-23} \text{ J K}^{-1}$) and Planck ($6.626 \times 10^{-34} \text{ J s}$) constants, respectively, while T_p denotes the temperature of maximum decomposition rate derived from the DTG curve.

The computed values of the thermodynamic parameters are presented in Table 2.

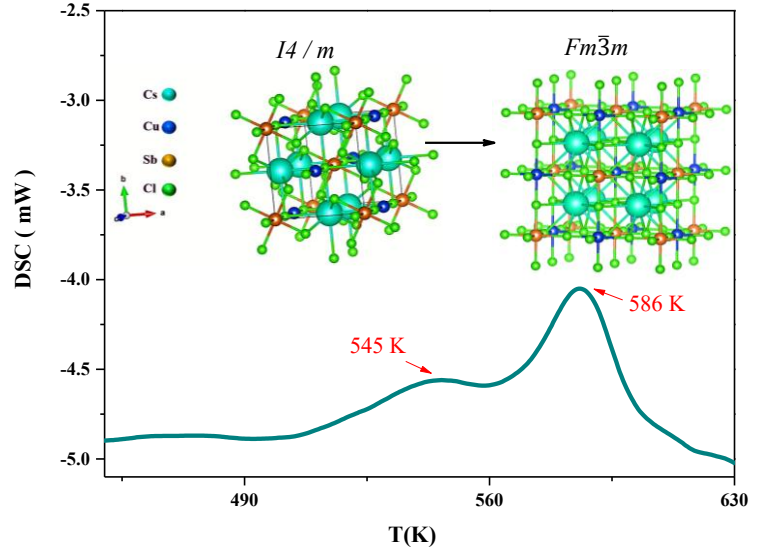
The table indicates that $\text{Cs}_2\text{CuSbCl}_6$ demonstrates moderate thermal stability when compared to other inorganic halide perovskites [39], [40]. Kluherz et al. predicted that $\text{Cs}_2\text{AgBiI}_6$ is thermodynamically unstable [28]. However, $\text{Cs}_2\text{NaBiBr}_6$ was determined to be intrinsically unstable and could not be synthesized; its chloride counterpart, $\text{Cs}_2\text{NaBiCl}_6$, successfully formed a stable cubic structure [41]. The E_a value obtained in this study is comparable to values reported for alternative 2D/3D perovskite solar cells [30], indicating that $\text{Cs}_2\text{CuSbCl}_6$ demonstrates excellent thermal stability and is thus suitable for optoelectronic applications. The positive ΔH value obtained for the II-decomposition stage indicates that degradation of the $\text{Cs}_2\text{CuSbCl}_6$ lattice is an endothermic process. This aligns with the requirement to supply thermal energy to sever the metal–halide (Sb–Cl and Cu–Cl) coordination bonds. The obtained ΔH value is close to that of the DPVs oxide $\text{La}_2\text{FeCrO}_6$, as reported by E. Ateia et al. [25], but slightly lower than that of the single HDPVs [29]. Conversely, the negative ΔS values suggest that the activated complex generated during decomposition exhibits a more ordered structure than the initial reactant. This is generally understood to indicate that the activated complex retains short-range order among the corner- and edge-sharing octahedra prior to the release of gaseous or volatile decomposition products, resulting in a loss of configurational freedom as the system approaches the transition state. Finally, the positive ΔG value confirms that the decomposition process is non-spontaneous under the given conditions and requires continuous external heat input to drive the breakdown observed in the TGA/DTG curves.

Table 2 Thermodynamic and kinetic parameters were determined for Phase II through TGA analysis of $\text{Cs}_2\text{CuSbCl}_6$.

Phase	T(K)	k (min^{-1})	$t_{1/2}$ (min)	E_a (kJmol^{-1})	ΔH (kJmol^{-1})	ΔS ($\text{Jmol}^{-1} \text{K}^{-1}$)	ΔG (kJmol^{-1})
II	512	0.08	8.7	29.1	24.8	-257.22	157

Furthermore, Fig. 6 shows the DSC thermogram of $\text{Cs}_2\text{CuSbCl}_6$. As the temperature increases, two distinct exothermic peaks appear, centered at 545 K and 586 K, with no corresponding mass loss observed in the TGA profile. This absence of mass loss indicates that the thermal anomalies arise from successive thermally induced structural rearrangements or phase transitions rather than chemical decomposition. These features may be attributed to changes in the tilting and distortion of the $[\text{CuCl}_6]$ and $[\text{SbCl}_6]$ octahedra, or to variations in cation/anion ordering within the double perovskite lattice. Comparable temperature-driven symmetry evolution has been reported for related HDPVs by King, Li et al. [30, 31], where thermally induced suppression of octahedral tilting drives a phase transition from the tetragonal $I4/m$ structure to the cubic $\text{Fm}\bar{3}m$ phase. Accordingly, the DSC peaks observed for the investigated sample can be attributed to successive lattice reorganizations toward a more symmetric configuration at elevated temperatures. This interpretation is further supported by the increase in estimated entropy values from 22.74 to 28.68 $\text{J mol}^{-1} \text{K}^{-1}$, which reflects greater vibrational and structural freedom in the higher-symmetry phase [32, 33].

Fig. 6. DSC graph of $\text{Cs}_2\text{CuSbCl}_6$. The inset reveals the structure diagrams of $\text{Cs}_2\text{CuSbCl}_6$.



3.2. Optical Properties

3.2.1. Diffuse reflectance spectroscopy (DRS)

The optical band energy gap (E_{bg}) of the Cl-DPVs is determined using the DRS. The measured reflectance spectra are converted into alternative absorption spectra by applying the Kubelka-Munk equation [31]:

$$F(R_{\infty}) = \frac{K}{S} = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \quad (12)$$

Where R_{∞} is the reflectance of an infinitely thick specimen, whereas K and S are the absorption and scattering coefficients, respectively. Replacing the absorption coefficient α in the Tauc equation [32] by $F(R_{\infty})$ provides:

$$[F(R_{\infty}).h\nu] = B (h\nu - E_{bg})^{\delta} \quad (13)$$

Here, B is an energy-independent constant, while $h\nu$ and E_{bg} represent the photon energy and band gap energy (eV), respectively. The exponent δ defines the nature of the optical transition, taking a value of 0.5 for direct allowed transitions or 2 for indirect allowed optical transitions [33]. The reflectance spectrum of HDPV shown in Fig.7a reveals a steep increase of light absorption in the visible region. Accordingly, the extrapolation of the linear portion of $[F(R) h\nu]^{1/\delta}$ versus $h\nu$ gives a direct E_{bg} of 1.2 eV, which is lower than that of comparable HDPVs such as $\text{Cs}_2\text{AgBiX}_6$ ($X = \text{Br}, \text{Cl}$) [34], [35]. The calculated band gaps are noted to be in proximity to the energy gaps (ranging from 1.2 eV to 1.4 eV) required for perovskite solar cells [28], [36].

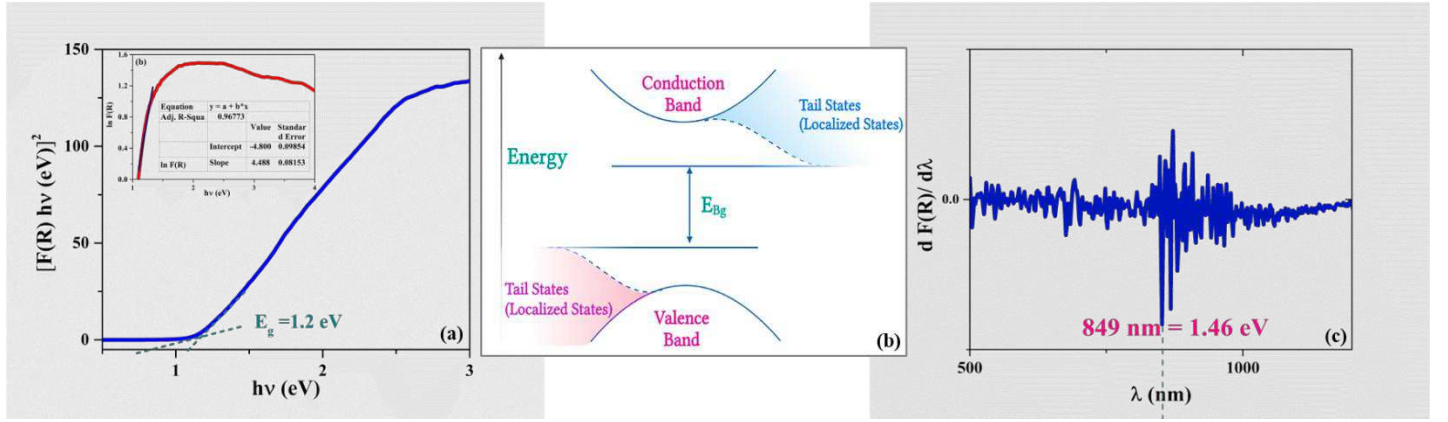


Fig.7. (a) Plot of $[F(R).hv]^2$ versus hv and the inset shows $\ln F(R)$ against hv of $\text{Cs}_2\text{CuSbCl}_6$ NPs. **(b)** Schematic representation of energy-band structure. **(c)** Plot of $d\alpha/d\lambda$ against wavelength (nm).

To further confirm the E_{bg} value, it was also evaluated using the Marotti method [37]. By plotting the first derivative of the absorption coefficient, $d\alpha/d\lambda$, over the 200–1100 nm wavelength range as illustrated in Fig. 7c, the E_{bg} is determined from the minimum of the $d\alpha/d\lambda$ plot. The corresponding value is approximately 1.46 eV. The reduced E_{bg} facilitates the absorption of photons with longer wavelengths, making $\text{Cs}_2\text{SbCuCl}_6$ a potential candidate for photovoltaic applications. Urbach energy (E_U) of the as-prepared NPs was determined using equation (14), by fitting the linear region of the plot $\ln F(R)$ versus hv [38], yielding a value of 0.22 eV as shown in the inset Fig. 7a.

$$\ln F(R) = \ln B + \frac{hv}{E_U} \quad (14)$$

Compared to the other lead-free HDPV, the E_U of $\text{Cs}_2\text{CuSbCl}_6$ is notably lower than those of $\text{Cs}_2\text{AgBiCl}_6$ (1.2 eV) and Cs_2SnCl_6 (0.425 eV) [39], [40]. This lower value suggests well-defined band-edge states and a reduced density of subgap trap states, both of which are beneficial for optoelectronic and photovoltaic performance [41]. Furthermore, the broadening of the optical absorption edge is commonly attributed to electron–phonon interactions and can be quantitatively described by the steepness parameter (σ), which is related to E_U through the following equation [45]:

$$\sigma = \frac{k_B T}{E_U} \quad (15)$$

Where k_B and T are assigned as the Boltzmann constant and absolute temperature, respectively.

The electron-phonon interaction (E_{e-ph}) is calculated as follows [42]:

$$E_{e-ph} = \frac{2}{3\sigma} \quad (16)$$

The steepness parameter (σ) was determined to be 0.117, resulting in a value of 5.67 for the electron-phonon interaction parameter.

3.2.2. Refractive index (n)

The refractive index (n) of HDPV is an essential optical parameter that reflects how light interacts with the material as it propagates through it. This index is affected by various factors, including composition, wavelength (λ), and crystal structure.

The value of n can be calculated using the equation (18) [43]:

$$n = \frac{1 + R}{1 - R} + \sqrt{\frac{4R}{(1 - R)^2} - k^2} \quad (17)$$

The optical dispersion of n of $\text{Cs}_2\text{CuSbCl}_6$ across the transparent region exhibits typical normal dispersion behavior as illustrated in Fig. 8a. The n decreases rapidly at shorter wavelengths before reaching a nearly constant value of approximately 1.77 at longer wavelengths. This value is comparable to other lead-free HDPVs but slightly lower than that of their Pb-based counterparts [44], [45].

3.2.3 Cauchy model

The Cauchy model elucidates the manner in which light of various wavelengths refracts to differing extents within a sample, while excluding the imaginary component. It is widely used to describe the optical behavior of dielectric and semiconductor materials where absorption is negligible. The optical dispersion of the n is fitted using the three-term Cauchy model:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (18)$$

As depicted in Fig. 8a, the experimental “n” data are fitted using nonlinear regression, yielding the parameters $A = 1.76$, $B = 2.55 \times 10^3 \text{ nm}^2$ and $C = 7.96 \times 10^9 \text{ nm}^4$. Parameter A represents the n at infinite λ , whereas the B and C coefficients confirm the normal dispersion behavior of the material in the transparent region [46]. As illustrated in Fig. 8a, the calculated n derived from the Cauchy model fitting demonstrates a significant correlation with the experimental data. Based on the Cauchy parameters, the calculated n varied from approximately 1.83 at 590 nm to 1.7 at 1500 nm, which is consistent with the optical behavior of HDPVs [47], [48], [49].

The high R^2 values suggest that the Cauchy model effectively characterizes the dispersion of n for the Cl-DPV sample. The Cauchy dispersion model contributes to the development and optimization of the sample studied for a range of applications, including photodetectors, light-emitting diodes, and solar cell devices [50], [51],[52].

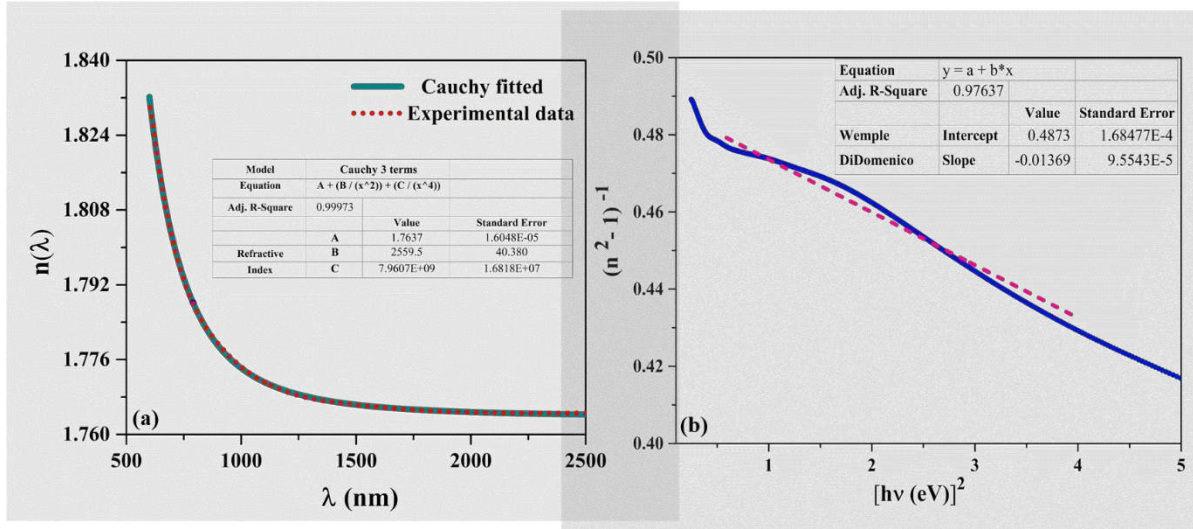


Fig.8. (a) Three-term Cauchy-fitted dispersion curve and (b) Plot of $1/(n^2-1)$ versus $h\nu$ for $\text{Cs}_2\text{CuSbCl}_6$.

3.2.4. Wemple-DiDomenico single oscillator model (WDM)

To gain further insight into the electronic polarization and inter-band transitions occurring inside the Cl-DPV, the WDM is applied. The model is given by equation (8):

$$(n^2 - 1)^{-1} = \frac{E_o}{E_d} - \frac{(h\nu)^2}{E_o E_d} \quad (19)$$

This model effectively explains the n dispersion observed below the inter band absorption edge, where $h\nu < E_{bg}$. It provides two key dispersion parameters, namely the single-oscillator energy (E_o) and dispersion energy (E_d), which reflect the electronic structure and strength of inter-band optical transitions [53]. These parameters are calculated by plotting $(n^2-1)^{-1}$ as a function of $(h\nu)^2$ as shown in Fig. 8b.

Additionally, the static refractive index (n_o) can be estimated from equation (19) by putting $h\nu = 0$ yielding the following equation [54]:

$$\epsilon_s = n_o = \left(1 + \frac{E_d}{E_o}\right)^{\frac{1}{2}} \quad (20)$$

The extracted values E_o , E_d , and n_o are 5.96, 12.24 eV, and 1.74, respectively. The relatively large value of E_d reflects strong electron-lattice interactions and significant orbital hybridization, which together give rise to multiple allowed optical transitions. The oscillator strength and effective oscillator energy reflect the combined influence of Cu-Cl-Sb bonding and localized electronic states, accounting for the material's strong optical response [6],[55].

The static dielectric constant (ϵ_s) was derived from the static refractive index (n_o) through the equation (20). Also, it can be estimated by extrapolating the real part of the dielectric constant to zero photon energy, yielding a value of 3.05 [56], as illustrated in Fig. 9a.

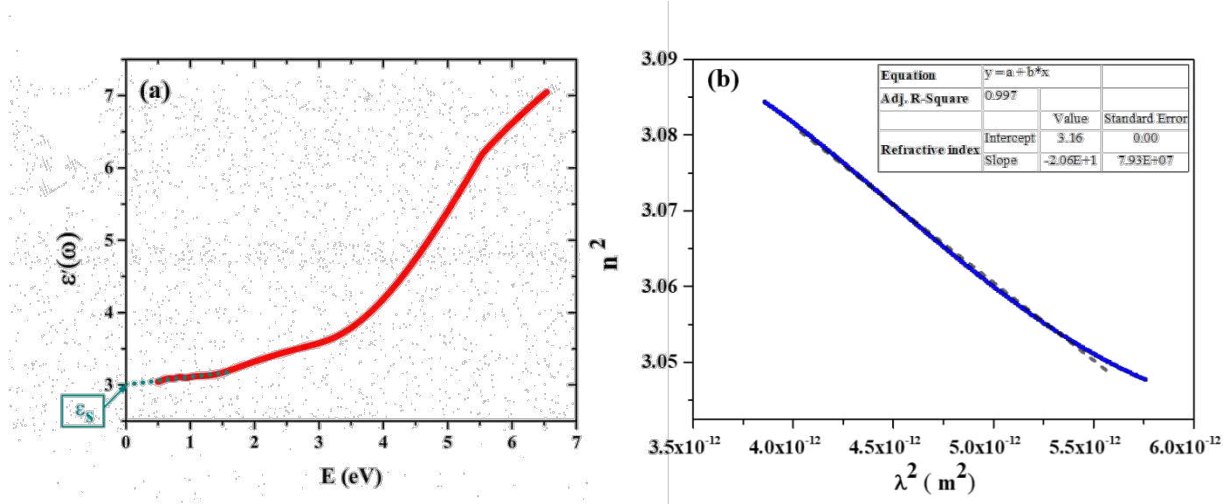


Fig.9. (a) Real part of dielectric constant (ϵ') as a function of energy (eV). **(b)** Plot of n^2 versus λ^2 for $\text{Cs}_2\text{CuSbCl}_6$ DPV.

The static dielectric constant (ϵ_s) describes the dielectric response of the CI-DPV at zero $h\nu$ and offers insights into its polarization and charge-screening properties. A comparatively high ϵ_0 implies greater electronic polarizability, less Coulombic interaction between charge carriers, potentially favorable for charge separation and improved light–matter interaction, which are advantageous features for the optoelectronic and photonic applications of CI-DPVs. Consequently, the derived ϵ_0 value underscores the promise of the studied CI-DPVs for use in photovoltaic devices and various optoelectronic systems. However, the earlier discussion can be summarized by stating that the Cauchy model gives an empirical representation of optical dispersion, whereas the WDM provides a deeper insight into electronic transitions by identifying E_0 and E_d . As a result, these two models collaborate to improve the characterization of the optical properties of CI-DPVs. The free carrier concentration (N) is a critical parameter governing the optoelectronic response of CI-DPVs, directly influencing electrical conductivity (σ) and dielectric polarization (P). Using the Drude Model given by equation [57]:

$$n^2 = \epsilon_L - \left[\left(\frac{e^2}{4\pi^2\epsilon_0 c} \right) \left(\frac{N}{m^*} \right) \right] \lambda^2 \quad (21)$$

where ϵ_L is the lattice dielectric constant, e is the elementary charge, ϵ_0 is the permittivity of free space, and c is the speed of light in vacuum. Figure 9b shows the dependence of n^2 on λ^2 . The ϵ_L is determined from the intercept of the straight line in the figure to be 3.16. For $\text{Cs}_2\text{CuSbCl}_6$, the ratio of carrier concentration to free carrier effective mass (N / m^*) is determined to be $2.46 \times 10^{50} \text{ Kg}^{-1} \text{ m}^{-3}$. The reported m^* typically ranges between $0.2 m_0$ and $0.8 m_0$, where m_0 is the free electron mass [58]. Using this range the free carrier concentration (N) is calculated to be $1.12 \times 10^{14} \text{ cm}^{-3}$. This result places CI-DPV $\text{Cs}_2\text{CuSbCl}_6$ in the semiconductor region (10^{17} - 10^{19} cm^{-3}), with a considerable carrier density [59]. This combination of moderate carrier density and low m^* enhances the material's compatibility for photovoltaic and optoelectronic devices, providing a balance between optical transparency and charge transport efficiency. The close agreement between ϵ_s (3.02) derived from the WDD model and ϵ_L (3.16) obtained from the Drude model confirms the consistency of the two optical dispersion approaches. This agreement indicates that the dielectric response is dominated mainly by bound electronic and lattice vibration contributions rather than by free-carrier

contributions [60]. Table 3 demonstrates a comparative overview of the optical and electronic parameters of various HDPVs. The comparison emphasizes the distinct optoelectronic characteristics of the studied $\text{Cs}_2\text{CuSbCl}_6$ when compared to other lead-free and Pb-based perovskite structures. In $\text{Cs}_2\text{CuSbCl}_6$, the electronic structure is dominated by the alternating Cu-Cl and Sb-Cl octahedral units, wherein the valence band maximum (VBM) is mainly originated from Cl orbitals and Cu-3d states. In contrast, the conduction band minimum (CBM) is principally constituted by Cl-2p and Sb-5p states [61],[6]. The pronounced hybridization within Cu-Cl-Sb bonding framework engenders the dispersive character in the CBM, thereby enhancing the ratio N/m^* which further modulates carrier mobility [62]. Moreover, the coexistence of localized states and polaronic effects is consistent with strong electron–lattice coupling, which shifts both the effective oscillator energy and the dispersion energy [66] to higher values, collectively reinforcing the exceptional optoelectronic properties of the present Cl-DPVs system.

Table 3 illustrates the bandgap E_{bg} , refractive index (n), Oscillator energy (E_o), Dispersion energy (E_d) and Carrier concentration (N) of various halide double perovskites.

Material	n	E_{bg} (eV)	E_o (eV)	E_d (eV)	$N(\text{cm}^{-3})$	Reference
$\text{Cs}_2\text{AgBiCl}_6$	2.0	1.95	7.5	~15-18	10^{13} - 10^{15}	[34]
$\text{Cs}_2\text{AgBiBr}_6$	2.1	1.95	7-8	~17-20	10^{14}	[59]
Cs_2ZrCl_6	1.7-1.8	3.0	8-9	~12-16	10^{13}	[35]
$\text{Cs}_2\text{CuSbCl}_6$	1.75-1.85	1.20	5.96	12.24	1.12×10^{14}	The present work

3.3. Mulliken electronegativity approach (M.E.A)

The Mulliken electronegativity (χ) serves as a useful method for estimating the valence band (V.B.) and conduction band (C.B.) edge positions. The χ value is related to the electron affinity (A_f), which describes an atom's tendency to form negative ions, and the first ionization potential (I_1), defined as the minimum energy required to remove the most loosely bound electron to form a positive ion, as illustrated by the equation below [14]:

$$\chi = \frac{1}{2}(A_f + I_1) \quad (22)$$

The parameter χ is calculated as the geometric-mean of the Pearson electro-negativities of the essential elements, as outlined in equation (23)[63]:

$$\chi_{\text{Mulliken}} = \chi_{\text{Pearson}} \quad \text{and} \quad \chi = \sqrt[N]{\chi_1^a \chi_2^b \chi_n^c} \quad (23)$$

In the compound, a , b , and c signify the number of atoms, while 1, 2, and n refer to the different categories of atoms; N is the total number of atoms [86]. The potentials of the conduction and valence bands E_{CB} and E_{VB} can be calculated from the following equations [86]:

$$E_{CB} = \chi - E_e - \frac{1}{2}E_{bg} \quad (24)$$

$$E_{VB} = E_{CB} + E_{bg} \quad (25)$$

The values of χ , band-edge positions for $\text{Cs}_2\text{CuSbCl}_6$ along with their E_{bg} , are presented in Table 4. In this context, the band-edge potentials of $\text{Cs}_2\text{CuSbCl}_6$ as shown in Fig.10 were determined using the M.E.A. The positions of the E_{CB} and E_{VB} were calculated to be +1.25 V and +2.45 V versus the Normal Hydrogen Electrode (NHE), respectively. The E_{VB} exceeds the redox potentials of $\text{H}_2\text{O}/\text{O}_2$ (+1.23 V) and $\text{OH}^-/\bullet\text{OH}$ (+1.99 V), indicating a strong oxidation capability. Conversely, the E_{CB} at +1.25 V vs NHE is relatively positive, rendering it unsuitable for the reduction of H^+ to H_2 , as hydrogen evolution necessitates an E_{CB} potential that is more negative than 0 V vs NHE, implying that $\text{Cs}_2\text{CuSbCl}_6$ is more advantageous for photocatalytic oxidation and pollutant degradation rather than for reduction.

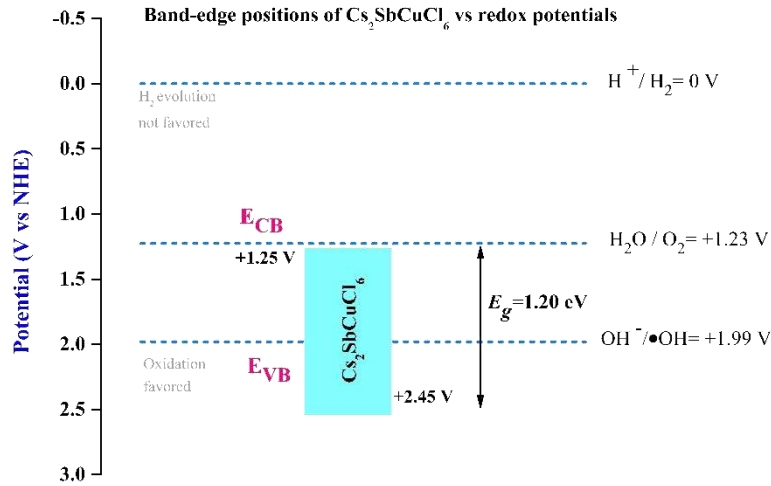


Fig. 10. Schematic representation of band-edge positions of $\text{Cs}_2\text{CuSbCl}_6$ vs normal Hydrogen electrode (NHE) scale.

Table 4 Comparison of χ , band-edge positions, and E_{bg} between the present work on $\text{Cs}_2\text{CuSbCl}_6$ and previous studies.

Parameters	χ (eV)	E_{CB} (eV)	E_{VB} (eV)	E_{bg} (eV)	E_{bg} Nature	References
$\text{Li}_2\text{GaInBr}_6$	5.77	-0.15	2.69	2.84	indirect	33
$\text{Rb}_2\text{AgBiCl}_6$	5.63	-0.28	2.575	2.86	indirect	34
$\text{Na}_2\text{GaInBr}_6$	5.84	0.42	2.25	1.83	indirect	33
$\text{Cs}_2\text{AgIn}_{0.75}\text{Bi}_{0.25}\text{Cl}_6$	---	-0.8	2.15	2.89	direct	[64]
$\text{Cs}_2\text{AgInCl}_6$	---	-0.87	2.65	3.53	direct	[64]
$\text{Cs}_2\text{CuSbCl}_6$	6.35	1.25	2.45	1.20	direct	Current study

Conclusion

Cs₂CuSbCl₆ double perovskite (Cl-DPV) nanoparticles were successfully synthesized via a straightforward precipitation route from an acidic solution. The structural, morphological, thermal, and optical properties were comprehensively investigated. X-ray diffraction affirmed the cubic perovskite symmetry with space group Fm $\bar{3}$ m, while HRTEM imaging verified the nanoscale morphology of the synthesized sample. Optical reflectance measurements revealed a narrow direct band gap of 1.2 eV, highlighting significant light-harvesting efficiency within the visible to near-infrared region. The pronounced orbital hybridization within the Cs₂CuSbCl₆ structure is expected to influence electronic band dispersion and, subsequently, charge carrier transport. In addition, the calculated free carrier concentration of $1.12 \times 10^{14} \text{ cm}^{-3}$ supports the semiconducting nature of the as-prepared Cl-DPV. Thermogravimetric analysis demonstrated good thermal stability for the Cs₂CuSbCl₆ nanoparticles, while the Wemple–DiDomenico (WDM) model enabled determination of the static refractive index, offering further insight into the optical quality and structural ordering of the material. Based on the Mulliken electronegativity approach, Cs₂CuSbCl₆ appears unsuitable for hydrogen reduction applications but shows promise for oxidation processes. Overall, the structural, optical, and thermal characteristics highlighted in this study underscore the potential applicability of Cs₂CuSbCl₆ for future optoelectronic devices.

Declarations

Data availability

All data supporting the findings of this study are included within the article.

Funding

The authors did not receive any support from any organization for the submitted work.

Author contributions

Ebtesam E Ateia contributed with conceptualization, validation, data gathering and analysis, writing and preparing the original draft, supervision, visualization, reviewing, and editing.

Dina Gawad contributed with conceptualization, validation, data gathering and analysis, writing and preparing the original draft, supervision, visualization, reviewing, and editing.

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Competing interest

The authors declare no competing interests.

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