

Article

Structural and Optical Effects of Zinc Halide Doping and Br[−]/I[−] Substitution in CsPbBr₃ Thin Films

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Abstract

This work reports the results of a study on the optical, morphological, and structural properties of cesium lead bromide iodide mixed perovskite thin films (CsPbBr_{3−x}I_x), synthesized by sequential evaporation of precursors (CsBr, PbBr₂, PbI₂). First, the deposition conditions were optimized to obtain thin films predominantly composed of the pure CsPbBr₃ phase. Subsequently, the influence of partial substitution of Br[−] by I[−] on the film properties was investigated. Particular emphasis was placed on evaluating the effect of partial Pb²⁺ substitution by Zn²⁺ on the optical, morphological, electronic, and structural properties using optical transmittance, photoluminescence, scanning electron microscopy (SEM), X-ray diffraction (XRD), Urbach energy analysis, and density functional theory (DFT) calculations. Zn²⁺-doped CsPbBr_{3−x}I_x films were prepared by evaporating a ZnBr₂ layer onto the pre-deposited PbBr₂/PbI₂ precursor layers. It was found that Zn²⁺-doped inorganic CsPbBr_{3−x}I_x perovskite films exhibit enhanced crystallinity and improved surface morphology. Additionally, photoluminescence characterization confirms that non-radiative recombination decreases significantly, apparently due to a reduction in intrinsic defect density. The effect of Zn²⁺ doping on the power conversion efficiency of carbon-based planar solar cells was also evaluated. Collectively, Urbach energy, photoluminescence, and SEM analyses revealed that the optimal Zn²⁺ doping range for CsPbBr_{3−x}I_x perovskite films is ≤5%.

Keywords: inorganic perovskite thin films; optical properties; solar cells



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1. Introduction

Organic–inorganic hybrid perovskite solar cells have been intensively investigated since their discovery, owing to their outstanding optoelectronic properties, including high absorption coefficients, long carrier diffusion lengths, low trap density, and ease of synthesis via solution growth and thermal evaporation [1–10]. These attributes have enabled remarkable efficiency improvements over the past decade, with single-junction perovskite devices now surpassing 26% and silicon-perovskite tandems exceeding 34% [11–15]. Despite these advances, critical challenges to the long-term stability of these devices continue to limit their practical application and commercialization.

This instability stems primarily from the volatility of the organic cations typically used in traditional organic–inorganic hybrid PSCs, which leads to poor moisture and thermal stability [16–18], thereby limiting their market adoption. To prevent this degradation, inorganic cesium ions (Cs^+) are used to replace the organic cations, allowing the manufacture of all-inorganic PSCs [19–21] with which conversion efficiencies exceeding 21% have been obtained [22]. Among all-inorganic PSCs, those based on CsPbI_3 , $\text{CsPbBr}_{3-x}\text{I}_x$, and CsPbBr_3 have experienced greater development [23]. It is worth noting that among all the studied all-inorganic perovskites, devices based on CsPbI_3 have achieved the highest PCE (over 21%). However, this exhibits severe degradation because the α - CsPbI_3 phase can only be stable above 330 °C, leading to its rapid conversion to the non-photoactive phase (δ - CsPbI_3) at room temperature [15,16]. On the contrary, CsPbBr_3 is a stable phase. Still, it has a bandgap of 2.35 eV, which limits its light-harvesting capability in the visible region, resulting in low photocurrent and, therefore, low conversion efficiency [17–19]. On the other hand, mixed-halide inorganic perovskites ($\text{CsPbI}_{3-x}\text{Br}_x$) offer improved absorption capacity and structural stability when a suitable ratio of halide anions is used. In particular, mixed-halide perovskites with an amount of iodine less than or equal to the composition CsPbIBr_2 ($E_g = 2.05$ eV) exhibit both better bandgap and phase stability, rendering them a good alternative for the fabrication of PSCs [22,23]. B-site doping with other metal ions has also been shown to be an effective method to improve the efficiency and stability of CsPbIBr_2 -based cells [24–27]. In particular, partial replacement of Pb^{2+} by Zn^{2+} has been successfully investigated in several inorganic perovskite materials [28–31].

In this study, special emphasis is placed on the influence that the partial substitution of the Pb^{2+} cation by Zn^{2+} has on the optical, morphological, structural, and electronic properties of cesium lead bromide iodide mixed perovskite thin films ($\text{CsPbBr}_{3-x}\text{I}_x$), synthesized by sequential evaporation of precursors (CsBr , PbBr_2 , PbI_2). This work contributes to the study of inorganic $\text{CsPbBr}_{3-x}\text{I}_x$ perovskite films by investigating the simultaneous incorporation of I and Zn through sequential evaporation. This reproducible and potentially scalable deposition route deserves further exploration.

Through XRD measurements, we have found that CsPbBr_3 films present good phase stability under normal humidity and lighting conditions. However, the $\text{CsPbBr}_{3-x}\text{I}_x$ films prepared with an amount of iodine greater than that corresponding to the composition CsPbBr_2I exhibit severe degradation associated with a transition from the α -phase to the non-photoactive δ -phase at room temperature. To avoid degradation under normal humidity and lighting conditions, samples with the composition $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ were prepared and exhibited good phase stability. These were characterized using XRD, SEM, photoluminescence, spectral transmittance, and Urbach energy measurements to evaluate the effect of Pb^{2+} substitution by Zn^{2+} on its optical, structural, morphological, and crystallographic properties. The influence of Zn^{2+} doping was also studied using DFT calculations. Therefore, the main contribution of this study lies in clarifying the composition–property relationships of Zn- and I-modified CsPbBr_3 films prepared by sequential evaporation.

2. Materials and Methods

$\text{CsPbBr}_{3-x}\text{I}_x$ thin films were prepared using a method consisting of the sequential evaporation of its precursors (PbBr_2 , PbI_2 , CsBr), deposited on a soda-lime glass substrate at room temperature from Knudsen cell crucibles at growth rates of around 5 Å/s. These are subsequently annealed under normal air conditions at temperatures ranging from 200 °C to 350 °C for 15 min. Good reproducibility of both the composition and properties of the evaluated samples was achieved using equipment with facilities to electronically control the evaporation temperature and deposition rate of precursors via Proportional–Integral–Derivative (PID) and Pulse Width Modulation (PWM) algorithms. Details of the

equipment used to prepare the $\text{CsPbBr}_{3-x}\text{I}_x$ films are described in a previously published paper (see Ref. [32]).

The chemical composition of the resulting compound was varied over a wide range by adjusting the thickness ratio of the precursors, which was determined using a thickness monitor. Initially, a 450 nm-thick layer of PbBr_2 was deposited, followed by consecutive deposition of the PbI_2 and CsBr layers. Through a study of parameters, conditions were found to produce $\text{CsPbBr}_{3-x}\text{I}_x$ films, with compositions ranging from $x = 0$ (CsPbBr_3) to $x = 2$ (CsPbBrI_2). The influence that the partial substitution of Pb^{2+} for Zn^{2+} (obtained by additional evaporation of a layer of ZnBr_2) produces on the optical, morphological, structural, and electronic properties of $\text{CsPbBr}_{3-x}\text{I}_x$ films was also studied. This study was performed using reference perovskite films with a $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ composition that exhibit good stability under humidity and ambient light.

The prepared samples were characterized by transmittance and reflectance measurements performed using a Varian–Cary 5000 spectrophotometer (Agilent Technologies, Inc., Santa Clara, CA, USA), as well as by XRD measurements performed with a Philips X'Pert Pro PANalytical diffractometer, using $\text{Cu K}\alpha$ radiation ($1.540598 \text{ \AA}$), an acceleration voltage of 40 kV, and a current of 40 mA. The film thickness was determined using a Maxtec TM-400 (Maxtek, Inc., Salt Lake City, UT, USA) thickness monitor, calibrated with a Veeco Dektak 150 surface profiler (Veeco Instruments Inc., Tucson, AZ, USA). The morphological characterization was performed using an SEM (TESCAN Vega 3, TESCAN Brno, s.r.o., Brno, Czech Republic).

The stoichiometry of the films obtained by sequential evaporation was carefully controlled by monitoring the deposited thickness of each precursor using a quartz crystal microbalance (QCM, Maxtek). The amounts of CsBr and PbBr_2 were calculated using their molar masses and densities to achieve a molar ratio close to 1:1, required for the formation of the CsPbBr_3 perovskite phase. In particular, the masses of CsBr and PbBr_2 used were nearly stoichiometric, minimizing the occurrence of cesium- or lead-rich conditions that could favor the formation of secondary phases, such as Cs_4PbBr_6 or residual PbBr_2 .

3. Results

3.1. Structural Properties Study

Initially, a study was conducted to identify synthesis conditions for growing thin films of CsPbBr_3 composition free of secondary phases. For this, the ratio of $\text{PbBr}_2/\text{CsBr}$ thicknesses was varied between 1:2.3 and 2.5:1, and the annealing temperature after deposition was set to room temperature. The crystalline phase in which these samples grew was established through XRD measurements.

Figure 1 shows the XRD patterns of the cesium lead bromide films with different thickness ratios of the precursors. This study showed that the obtained samples consisted of a mixture of different phases, including cubic and orthorhombic CsPbBr_3 phases, as well as secondary phases of other ternary compounds. The diffractograms shown in Figure 1 reveal that the films deposited using a thickness ratio r of 1.5:1 grow only in the orthorhombic CsPbBr_3 phase (ICDD 01-087-4957), whereas films deposited with an excess of CsBr ($r = 1:2.3$ ratio) grow with a mixture of the orthorhombic CsPbBr_3 phases and the secondary Cs_4PbBr_6 phase (ICDD01-086-3013). On the other hand, films deposited with an excess of PbBr_2 ($r = 2.5:1$ ratio) result in samples that include a mixture of the orthorhombic CsPbBr_3 and CsPb_2Br_5 phases (ICDC 04-024-4338). Other authors have reported similar results [33,34]. The following reactions can describe the formation of CsPb_2Br_5 and Cs_4PbBr_6 [35]:



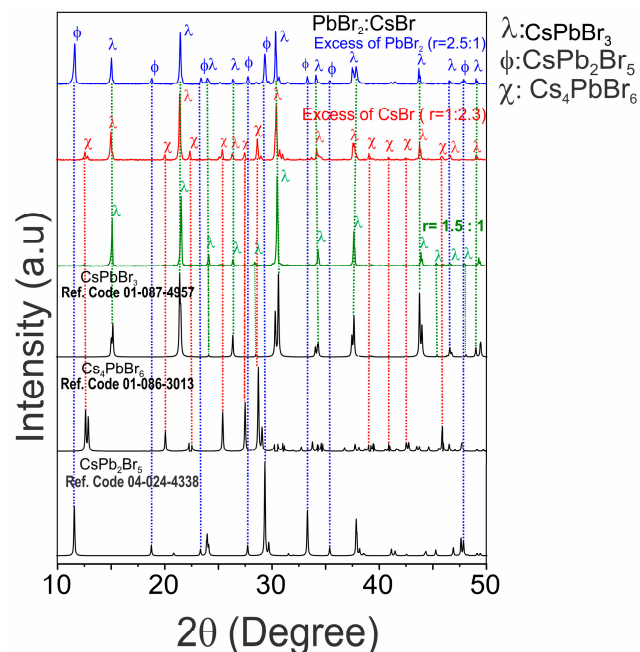
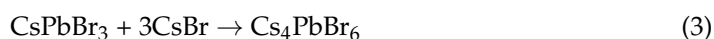
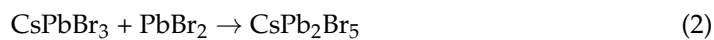


Figure 1. X-ray diffraction patterns of perovskite thin films deposited at room temperature by sequential evaporation of their precursors ($\text{PbBr}_2/\text{CsBr}$), varying the $\text{PbBr}_2/\text{CsBr}$ thickness ratio.

After deposition of perovskite films grown with a single-phase CsPbBr_3 , they were subjected to annealing in air at temperatures ranging between 220 °C and 350 °C, in an attempt to improve their properties. Figure 2 shows diffractograms of CsPbBr_3 thin films annealed in air at temperatures ranging from room temperature (without annealing) to 350 °C, for 15 min. The XRD pattern displayed in Figure 2 reveals that the post-thermal treatment does not affect the crystalline structure of the perovskite films. However, increasing the annealing temperature increases the intensity of the reflections, apparently associated with an improved degree of ordering of the crystallographic planes.

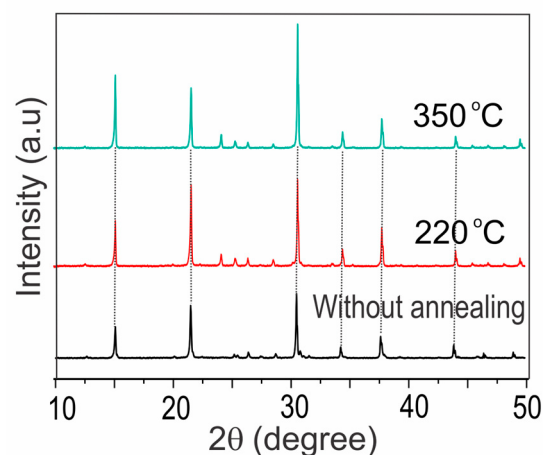


Figure 2. XRD patterns of CsPbBr_3 thin films annealed at different temperatures in air.

Once secondary-phase-free CsPbBr_3 thin films were obtained, a study was carried out to prepare $\text{CsPbBr}_{3-x}\text{I}_x$ thin films by partially replacing the Br^- anion with iodine in CsPbBr_3 films, following the methodology described above.

In Figure 3a, the XRD patterns of $\text{CsPbBr}_{3-x}\text{I}_x$ films prepared by varying the molar ratio x between $x = 0$ and $x = 2$ are displayed. These results reveal that CsPbBr_3 ($x = 0$) films exhibit only reflections corresponding to the orthorhombic phase of CsPbBr_3 , and when the iodine content increases in the $\text{CsPbBr}_{3-x}\text{I}_x$ sample, the crystalline structure does not change. However, the reflections observed in the XRD pattern shift towards lower 2θ values as the iodine concentration increases. This is an expected behavior, taking into account that iodine has an ionic radius greater than that of bromine, which leads to an expansion of the $\text{CsPbBr}_{3-x}\text{I}_x$ crystal lattice when the Br^- anion is replaced by I^- . This expansion of the lattice leads to an increase in the lattice constant, which is manifested in a displacement of diffraction peaks.

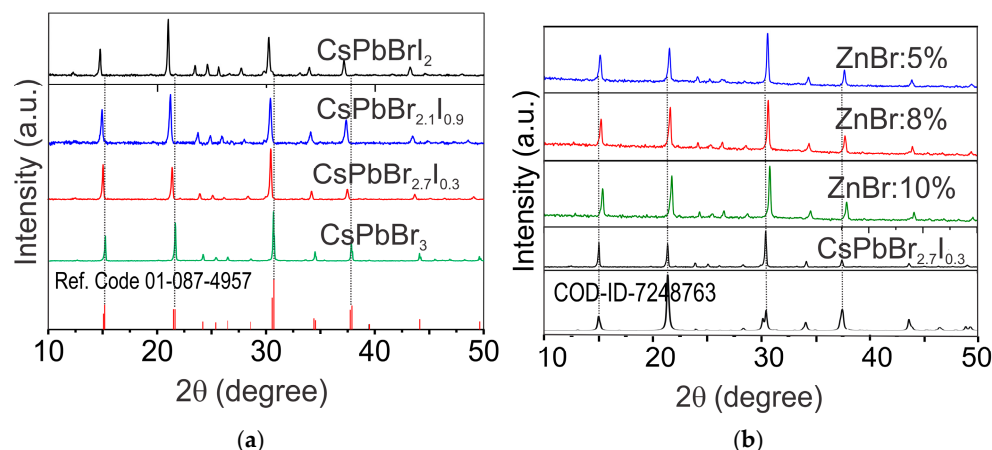


Figure 3. (a) XRD patterns of $\text{CsPbBr}_{3-x}\text{I}_x$ films, prepared by varying the molar ratio x between $x = 0$ and $x = 2$. (b) XRD pattern of $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ films doped with Zn^{2+} at atomic percentages ranging from 0% to 10%.

Figure 3b compares the XRD spectrum of the reference $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ sample with those in which Zn^{2+} replaces the cation Pb^{2+} in an atomic percentage that varied between 0% and 10%. These results reveal that $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ exhibits only reflections corresponding to the orthorhombic phase, and when Zn^{2+} ions substitute the Pb^{2+} cation, the crystalline structure does not change. However, the reflections observed in the XRD pattern shift towards larger 2θ values when the percentage of substitution of Pb^{2+} by Zn^{2+} increases. This shift is because the ionic radius of Zn^{2+} is smaller than that of Pb^{2+} , which causes a reduction in the size of the unit cell, and according to Bragg's law ($n\lambda = 2d \sin\theta$), for the relationship to be preserved, the angle θ must increase.

In this growth methodology, the precursors are initially deposited as independent layers, and subsequent heat treatment is therefore necessary to promote interdiffusion among the constituents and to favor the solid-state reaction that forms the perovskite phase. Temperatures above 130 °C were found to facilitate precursor diffusion, improve film crystallinity, and promote complete reaction between the different deposited species, particularly in the mixed-halide (Br/I) and Zn-incorporated compositions studied in this work.

Regarding the observed crystalline phase, it should be noted that CsPbBr_3 transitions to a cubic phase at elevated temperatures during heating. However, X-ray diffraction analyses were performed after the samples had cooled to room temperature. Under these conditions, CsPbBr_3 typically undergoes a return transition to the orthorhombic phase, which is the thermodynamically stable phase at room temperature. Therefore, although the films were annealed at temperatures above 130 °C, the observation of an orthorhombic structure in the XRD patterns is consistent with the expected behavior for this type of material after cooling. Additionally, the incorporation of iodine and zinc may slightly

modify the lattice parameters, structural distortion, and phase-transition temperature, thereby stabilizing the orthorhombic structure observed at room temperature.

3.2. Optical Properties Study

Typical transmittance, reflectance, and $(\alpha h\nu)^2$ vs $h\nu$ curves of CsPbBr₃ thin films deposited under optimal conditions are displayed in Figure 4. The absorption coefficient α was determined from the transmittance T and reflectance R curves, using the following relationship [36].

$$\alpha = \frac{1}{d} \left[\ln \left(\frac{T}{1-R} \right) \right] \quad (4)$$

The value of the energy gap E_g is obtained from the intercept with the $h\nu$ axis of the curve of $(\alpha h\nu)^2$ vs $h\nu$ (tauc curve).

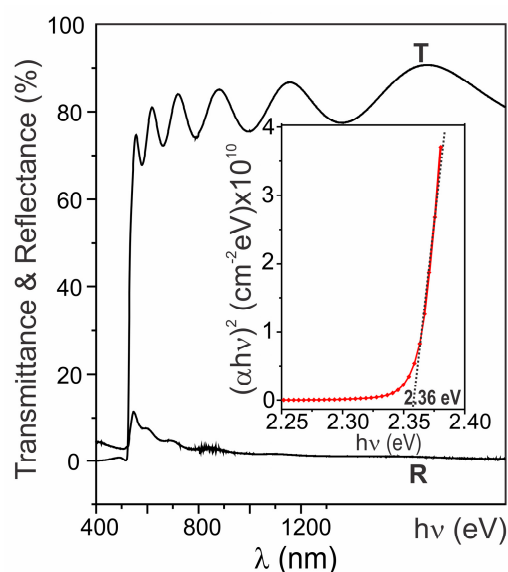


Figure 4. Transmittance, reflectance, and $(\alpha h\nu)^2$ vs $h\nu$ curves of a typical CsPbBr₃ thin film deposited by sequential evaporation.

The transmittance curves were found to have a steep slope near the cut-off wavelength (the edge of the conduction band), indicating that, in these samples, photon absorption occurs predominantly through fundamental absorption, which induces band-to-band carrier transitions. From this behavior, it can be concluded that the CsPbBr₃ films deposited by sequential evaporation exhibit a low density of states arising from native defects. On the other hand, the annealing temperature did not affect the energy gap of the CsPbBr₃ films. However, the thermal post-treatment slightly affects the transmittance intensity, apparently due to increased roughness induced by increased grain size.

The influence of the molar ratio x on the optical properties of CsPbBr_{3-x}I_x films was also studied by spectral transmittance and reflectance measurements. Typical transmittance and reflectance spectra of CsPbBr_{3-x}I_x are shown in Figure 5a. Moreover, the α vs. $h\nu$ and $(\alpha h\nu)^2$ vs. $h\nu$ curves (Tauc curves) are shown in Figure 5b and Figure 5c, respectively. By plotting $\ln(\alpha)$ vs. $h\nu$, the Urbach energy value can be determined from the slope of the curves. Figure 5d shows $\ln(\alpha)$ vs. $h\nu$ curves (near the band edge) for samples prepared with different molar ratios x , indicating the E_U value calculated from their respective slopes.

It is observed from the Tauc plots in Figure 5c. that the energy gap E_g of CsPbBr_{3-x}I_x films decreases from 2.35 eV to 1.91 eV when iodine substitution increases its molar concentration from $x = 0$ to $x = 2$. Smaller band gap values are advantageous for fabricating

solar cells with higher efficiency. However, when Br is excessively substituted by I, the perovskite films rapidly degrade into a non-photosensitive phase.

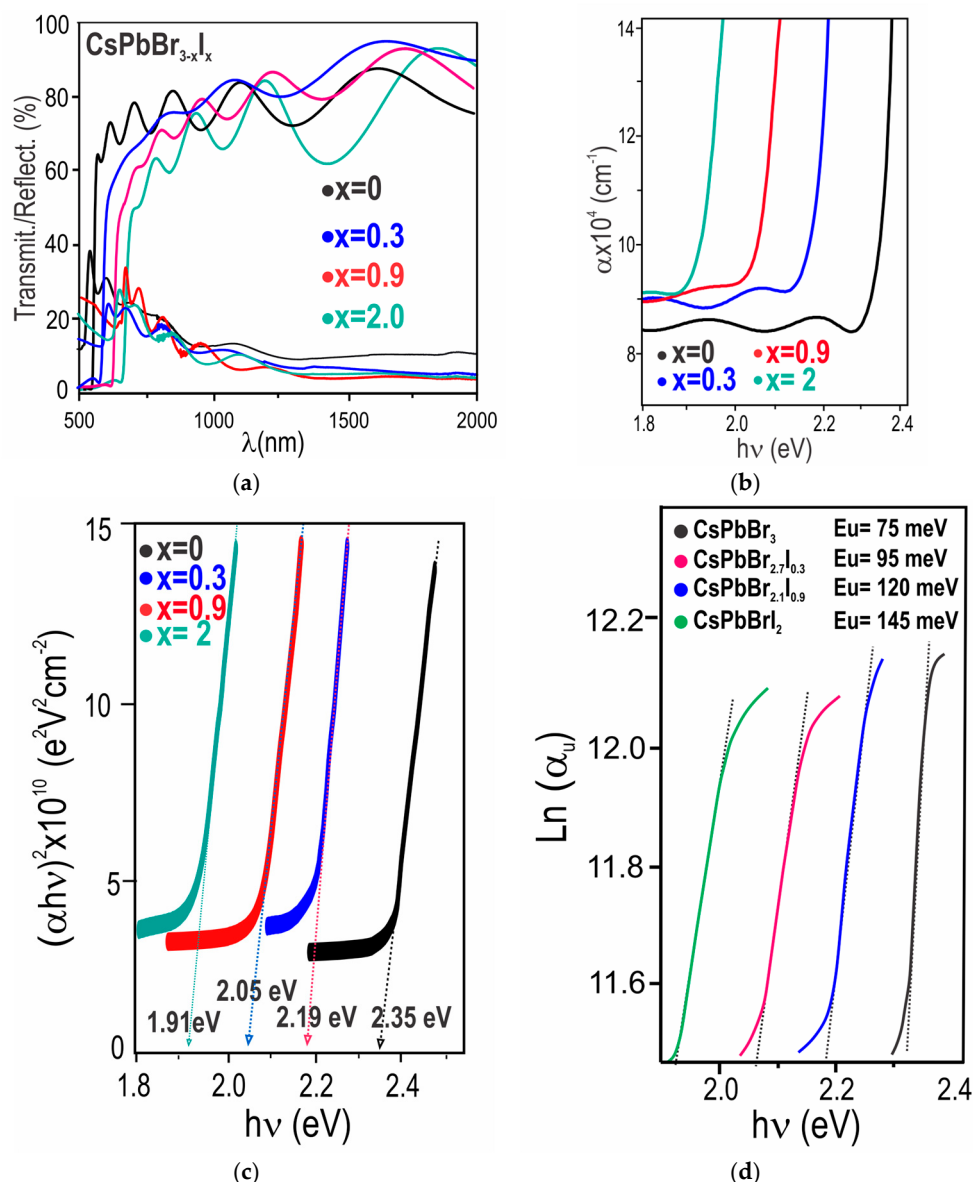


Figure 5. (a) Transmittance and reflectance spectra of CsPbBr_{3-x}I_x thin films prepared with different molar ratios x . (b) α vs. $h\nu$ curves. (c) $(\alpha h\nu)^2$ vs. $h\nu$ curves, corresponding to the Tauc plots used to estimate the optical band gap, as indicated by the dotted lines. (d) Near-band-edge $\ln(\alpha)$ vs. $h\nu$ curves used to determine the Urbach energy EU for CsPbBr_{3-x}I_x films with different molar ratios x . The optical band gap is indicated by the dotted lines.

It is also observed in Figure 5a that the slope of the transmittance curves decreases with increasing substitution of Br by iodine in CsPbBr_{3-x}I_x films. This behavior is associated with the formation of structural defects that lead to band distortion, generating state tails that extend the bands within the band gap, inducing a decrease in the slope of the transmittance curves. Therefore, the absorption via transitions between band tail states indicates how much structural disorder (stress and dislocation) can influence the optical properties. The absorption coefficient near the band edge (α_u), which is mainly influenced by absorption in band tail states, can be determined using the Urbach relation (Equation (5)) [37].

$$\alpha_U = a_0 \exp \exp \left[\frac{h\nu - E_i}{E_U} \right] \quad (5)$$

where E_i and α_0 are constants and E_U is the Urbach energy.

Considering that the Urbach energy is related to the density of states located in the band gap induced by structural disorder, the results in Figure 5d reveal that increasing iodine concentration leads to an increase in the Urbach energy, indicating that an increase in the density of structural defects is induced by the incorporation of iodine into the perovskite structure, apparently because the ionic radius of iodine (2.2 Å) is larger than that of bromine (1.96 Å) [38].

The influence of partial substitution of the Pb^{2+} cation by Zn^{2+} ions on the optical properties of a sample with the composition $\text{CsPbBr}_{3-x}\text{I}_x$ was also studied. Figure 6a shows typical transmittance and reflectance spectra and the corresponding Tauc curves for a reference film with composition $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ in which Pb^{2+} was substituted by Zn^{2+} at atomic percentages ranging from 0% to 13%. Figure 6b presents the corresponding $\ln(\alpha)$ vs. $h\nu$ curves near the band edge, used for estimating the Urbach energy.

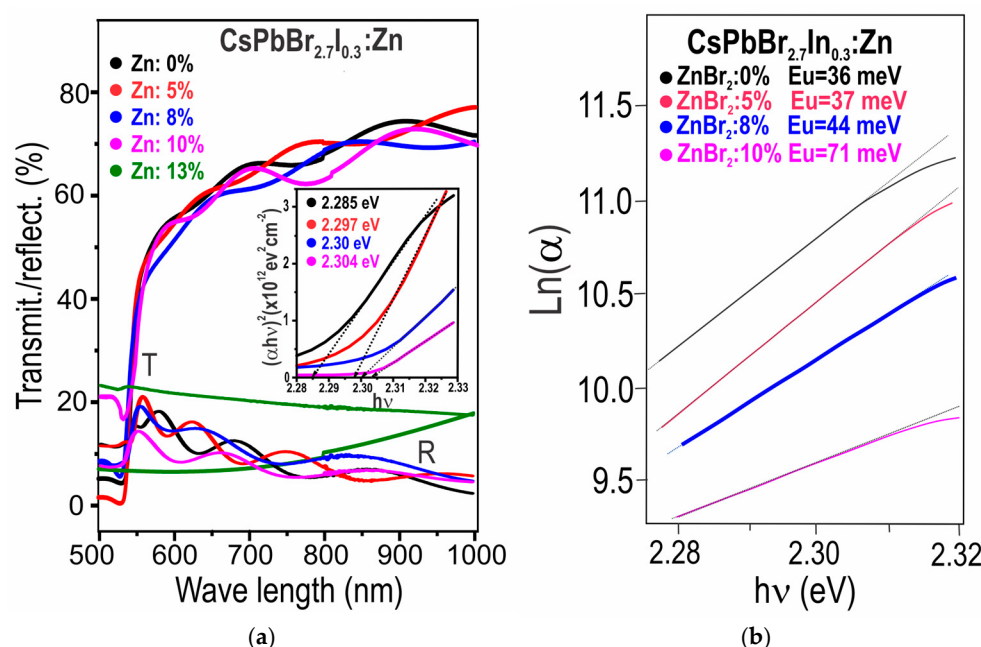


Figure 6. (a) Curves of transmittance and reflectance corresponding to a reference sample with composition $\text{CsPbBr}_{2.7}\text{I}_{0.3}$, to which the Pb^{2+} cation was replaced by Zn^{2+} in different atomic percentages. The inset shows the corresponding Tauc plots, with the optical band gap indicated by the dotted lines. (b) Curves of $\ln(\alpha)$ vs. $h\nu$ showing the Eu values obtained for a reference sample with composition $\text{CsPbBr}_{2.7}\text{I}_{0.3}$, doped with Zn^{2+} in different atomic percentages. The Eu values shown at the top of the graph were obtained from the slope of the dotted linear fits.

The results in Figure 6a show that replacing Pb^{2+} with Zn^{2+} at low concentrations has little effect on the energy gap of the studied sample, indicating that, under these conditions, the band structure is slightly affected. However, when the substitution of Pb^{2+} with Zn^{2+} is high (greater than 10%), the transmittance decreases strongly. No maximum and minimum are observed due to interference effects, indicating that these types of samples have a high degree of crystalline disorder, which gives rise to a high dispersion of incident radiation that destroys the coherence of the rays that overlap to generate constructive interference. On the other hand, it is observed that the slope of the transmittance curves of the samples with low Pb^{2+} substitutions by Zn^{2+} ($\leq 5\%$) is slightly affected. However, when the Pb^{2+} replacement percentage exceeds 6%, the slope decreases more sharply. This behavior can

be explained by considering that the replacement of Pb^{2+} by Zn^{2+} generates structural defects because the ionic radius of the Pb^{2+} (1.2 Å) is much larger than that of Zn^{2+} (0.74 Å). This situation generates band states within the gap, causing a decrease in the slope of the transmittance curves.

Figure 6b displays curves of $\ln(\alpha)$ vs. $h\nu$ (near the edge of the band) of a sample with composition $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ to which Zn^{2+} replaced the cation Pb^{2+} in an atomic percentage that varied between 0% and 10%. The Eu value calculated from the slope of the $\ln(\alpha)$ vs. $h\nu$ curves proved to be less than 44 meV for samples in which Pb^{2+} was replaced by Zn^{2+} at a percentage $\leq 8\%$, indicating that they exhibit good crystalline quality. On the contrary, when a Pb^{2+} replacement is made with a percentage of $\text{Zn}^{2+} \geq 8\%$, the Eu value increases significantly, indicating that, in this case, there is high structural disorder.

The influence of both the molar ratio x and the partial substitution of the Pb^{2+} cation by Zn^{2+} on the photoluminescence (PL) emitted by $\text{CsPbBr}_{3-x}\text{I}_x$ thin films excited with a 400 nm laser was also evaluated in this study. In Figure 7, PL spectra of $\text{CsPbBr}_{3-x}\text{I}_x$ thin films prepared with different molar ratios x and doped with Zn at different atomic percentages are displayed.

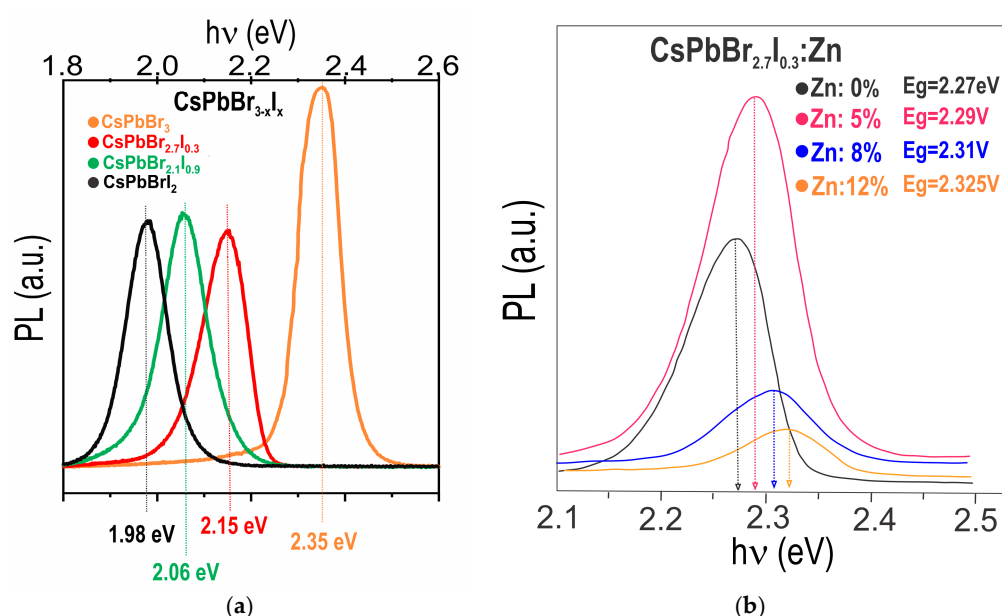


Figure 7. Photoluminescence spectra of: (a) $\text{CsPbBr}_{3-x}\text{I}_x$ thin films, prepared with different molar ratios x , and (b) a reference sample with composition $\text{CsPbBr}_{2.7}\text{I}_{0.3}$, doped with Zn in atomic percentages, varying between 0 and 12%. The optical band gap is indicated by the dotted lines in both graphics.

The results of Figure 7a show that an increase in the substitution of Br by iodine induces a reduction in the energy gap E_g from 2.35 eV ($x = 0$) to 1.98 eV ($x = 2$), in agreement with results reported by other authors [39,40] and with those previously obtained from Tauc curves. On the other hand, the PL spectra are symmetric, indicating that the radiative emission is primarily due to fundamental transitions between the valence and conduction bands. It is also observed that the CsPbBr_3 sample exhibits a PL intensity that is significantly higher than that of the other $\text{CsPbBr}_{3-x}\text{I}_x$ samples. This behavior could be explained by assuming that substituting iodine for Br in the CsPbBr_3 film generates non-radiative recombination centers associated with deep emission levels. Poor crystalline ordering in this type of sample could also contribute to the reduction in PL intensity.

It can also be observed in Figure 7b that the PL spectra of films prepared by substituting Pb^{2+} with Zn^{2+} at Zn^{2+} concentrations below 6% are quite symmetrical. Still, this symmetry

is lost when Zn^{2+} substitution exceeds 6% by atomic percentage. This behavior could be explained by assuming that the emission produced by samples prepared by substituting Pb^{2+} for Zn^{2+} at concentrations below 6% is primarily due to fundamental transitions between states in the conduction and valence bands. In comparison, films prepared with higher Zn^{2+} percentages emit, in addition to fundamental radiation, radiation induced by transitions involving energy levels within the band gap. These additional emission features may be associated with native defects, impurities, local compositional fluctuations, partial halide segregation, or slightly different compositional domains with distinct band gap energies. Although no clear secondary crystalline phases were detected by XRD, the presence of local compositional heterogeneities cannot be completely ruled out.

It is also observed that $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ films prepared by substituting Pb^{2+} with high atomic percentages of Zn^{2+} exhibit PL spectra with very low intensity. This behavior could be explained by poor crystalline quality and by the generation of non-radiative recombination centers associated with deep emission levels, induced by the excess substitution of Pb^{2+} by Zn^{2+} .

3.3. Morphological Properties Study

The influence that the partial substitution of Br^- by iodine and of Pb^{2+} by Zn^{2+} in the crystal structure of CsPbBr_3 thin films, as well as the post-deposition annealing in air, produces on the morphological properties of $\text{CsPbBr}_{3-x}\text{I}_x$ thin films was also studied by SEM measurements. Initially, the effect of annealing temperature (in air between 20 °C and 350 °C, for 15 min) on the morphology of single-phase grown CsPbBr_3 thin films was studied. Figure 8a shows the SEM image of an unannealed CsPbBr_3 thin film, and Figure 8b shows the SEM image of a sample annealed at 350 °C for 15 min; in Figure 8c, the grain size variation of CsPbBr_3 films annealed at temperatures between 20 °C and 350 °C. The grain size was calculated from the SEM micrographs using the linear intercept method [41] in ImageJ software, version 1.54g.

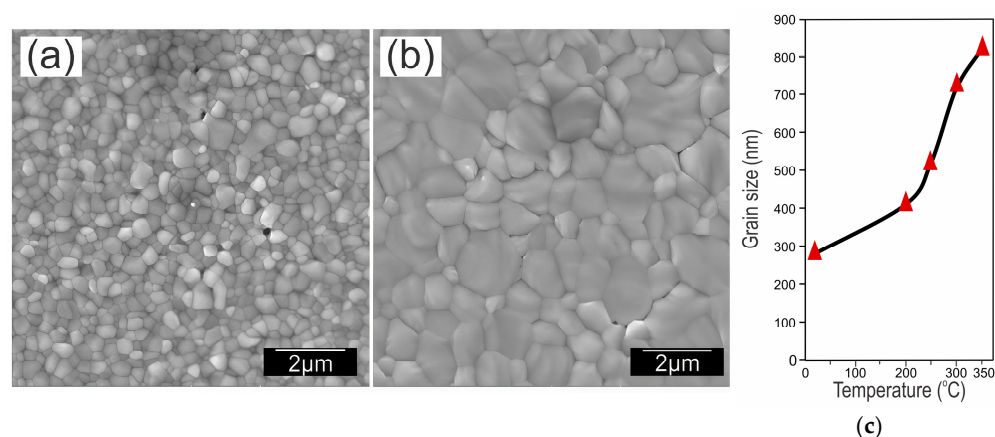


Figure 8. SEM images of: (a) unannealed CsPbBr_3 thin film, (b) sample annealed at 350 °C for 15 min. (c) grain size variation of CsPbBr_3 films annealed at temperatures between 20 °C, and 350 °C.

The SEM images in Figure 8 show that the CsPbBr_3 films generally have a morphology consisting of compact, pore-free spherical grains, resulting in excellent coverage of the entire substrate. It is also observed that the grain size increases significantly with annealing temperature, from average values close to 280 nm to grain sizes on the order of 820 nm. This behavior is attributed to a morphological change induced by an increase in annealing temperature.

After evaluating the effect of the annealing temperature, the influence of Br^-/I^- substitution on the film morphology was analyzed. Figure 9 shows SEM micrographs

of $\text{CsPbBr}_{3-x}\text{I}_x$ samples prepared with molar ratios ranging from $x = 0$ to $x = 2$. These results reveal that all the studied samples exhibit a compact morphology composed of submicrometric, nearly spherical grains. As the iodine content increases from $x = 0$ to $x = 2$, the average grain size decreases from $0.82 \mu\text{m}$ for CsPbBr_3 films (Figure 9a) to $0.50 \mu\text{m}$ for CsPbBrI_3 films (Figure 9d).

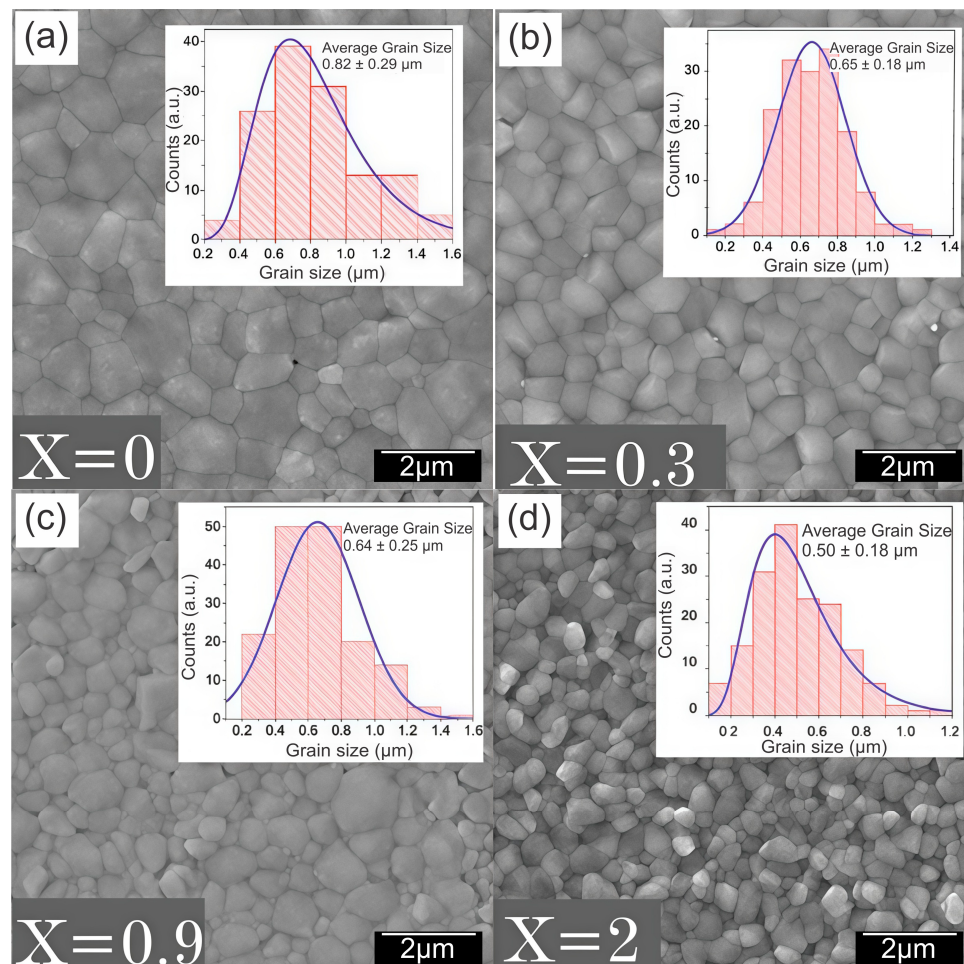


Figure 9. SEM images of $\text{CsPbBr}_{3-x}\text{I}_x$ thin films with molar ratios corresponding to: (a) $x = 0$, (b) $x = 0.3$, (c) $x = 0.9$, (d) $x = 2$.

The replacement of the Pb^{2+} cation by Zn^{2+} ions in inorganic $\text{CsPbBr}_{3-x}\text{I}_x$ perovskite films is a strategy that has been used effectively to improve both the crystallinity and morphology of this type of compound, as well as the efficiency and stability of cells based on inorganic perovskites [26,30]. In this work, the effect that the replacement of Pb^{2+} by Zn^{2+} has on the morphological properties of $\text{CsPbBr}_{3-x}\text{I}_x$ thin films was studied. This study was conducted using a reference sample with molar composition $x = 0.3$ ($\text{CsPbBr}_{2.7}\text{I}_{0.3}$). Figure 10 shows SEM micrographs of the reference sample in which Pb^{2+} was replaced by Zn^{2+} at atomic percentages ranging from 0% to 10%. These results reveal that the sample not doped with Zn exhibits a compact, small-grain morphology, and that when the cation Pb^{2+} is replaced by Zn^{2+} at low atomic percentages, the grain size increases significantly. When the Pb^{2+} cation in thin films of $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ is substituted in atomic percentages around 5%, samples with grain sizes of $1.33 \mu\text{m}$ are obtained. Still, when the Pb^{2+} cation is replaced by Zn^{2+} in atomic percentages greater than 8%, their morphology deteriorates significantly. These samples show a morphology characterized by the disappearance of the granular structure and the appearance of large islands, with a high density of voids.

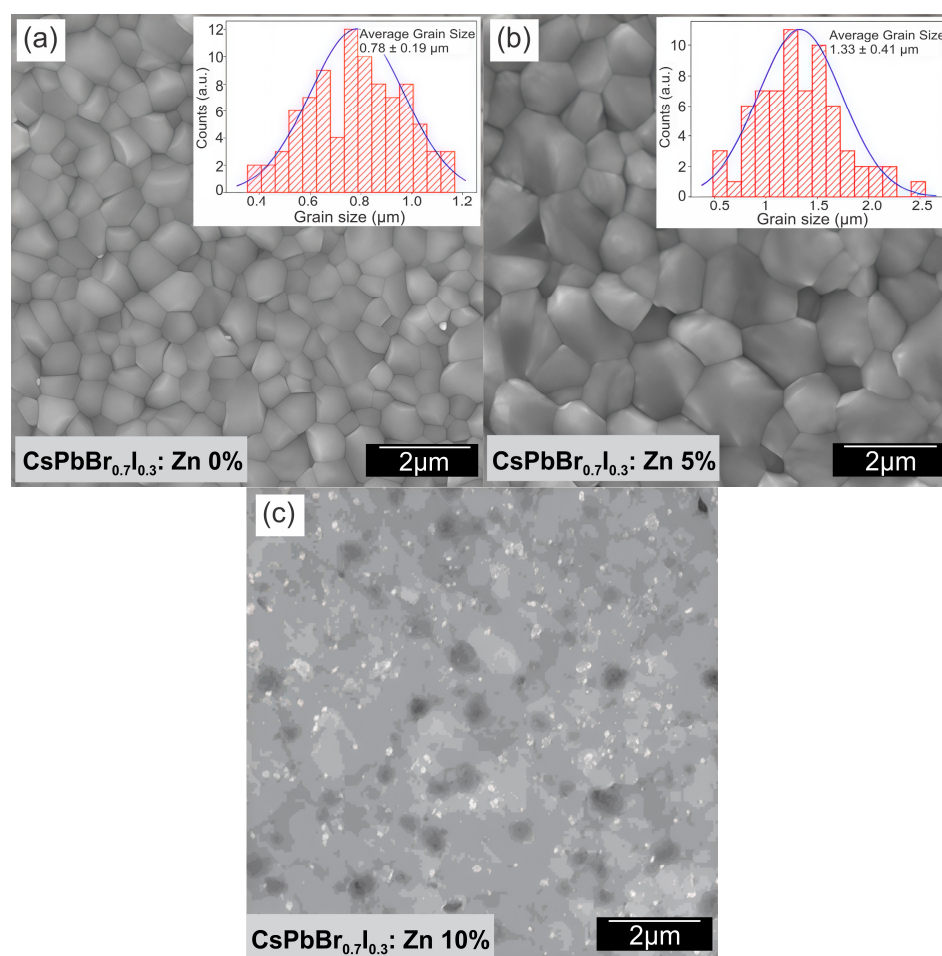


Figure 10. SEM images of a thin film of $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ in which Pb was partially replaced by Zn^{2+} at atomic percentages of: (a) 0%, (b) 5%, and (c) 10%.

EDX analysis (TESCAN VEGA SEM + EDX) confirmed the incorporation of zinc into the film structure, revealing an experimental concentration of approximately 0.45 wt% Zn (see Figure 11). This result is consistent with the nominal composition used during synthesis, corresponding to a 5% addition of ZnBr_2 relative to the Pb content. Considering the total mass of the perovskite and the contributions of the other elements present (Cs, Pb, Br, and I), the expected theoretical Zn content is around 0.5 wt%. Therefore, the agreement between the experimental and theoretical values confirms the effective incorporation of Zn into the synthesized material.

3.4. Influence of the Partial Substitution of the Cation Pb^{2+} by Zn^{2+} and the Anion Br by Iodine on the Band Structure of CsPbBr_3 Films

The influence of the partial substitution of the Pb^{2+} cation by Zn^{2+} and the Br^- anion by iodine on the band structure of CsPbBr_3 perovskites was analyzed through DFT computational calculations. To that end, from the x-ray diffraction patterns of the synthesized films, a supercell was constructed with two types of substitution: 5% of the Pb^{2+} cation sites by Zn^{2+} and the Br anion by iodine in a ratio $x = 0.3$ ($\text{CsPbBr}_{2.7}\text{I}_{0.3}$). The minimal supercell corresponded to a $3 \times 2 \times 1$ expansion of the primitive cell, with a total of 120 atoms. The configuration with the largest spacing between iodine atoms was selected to approximate a homogeneous distribution, and the most central Pb atom was substituted to minimize periodic interactions.

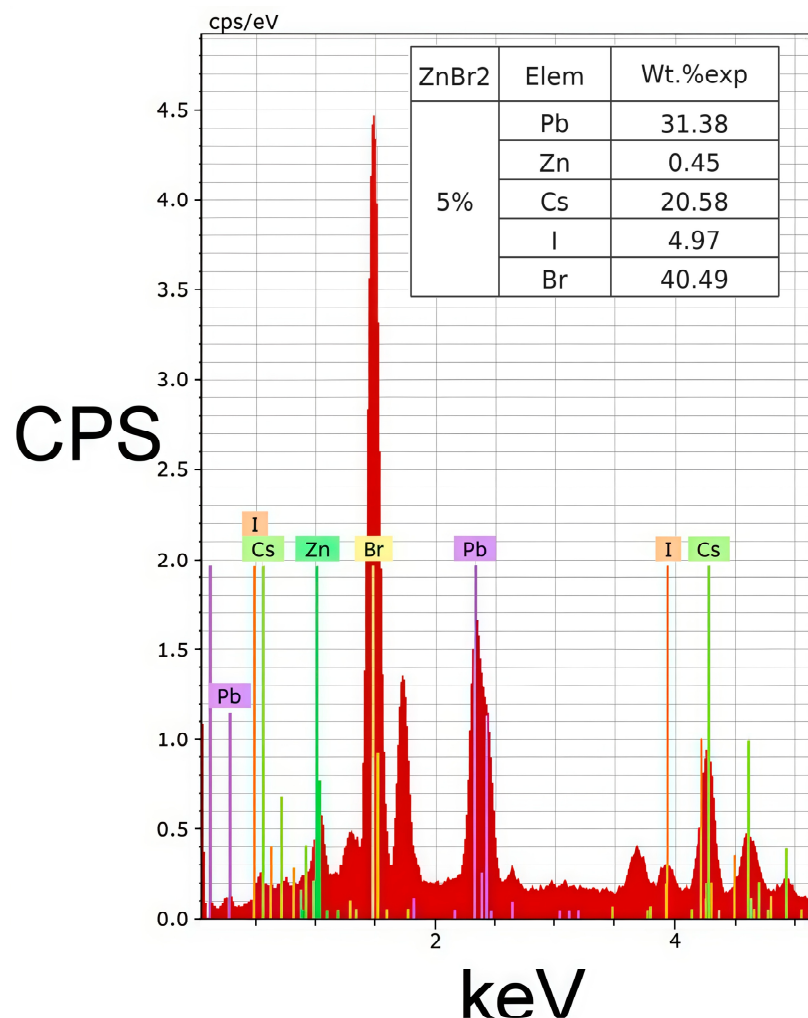


Figure 11. EDX spectrum of a $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ thin film in which Pb^{2+} was partially replaced by Zn^{2+} at an atomic percentage of 5%.

Structural relaxation was performed using pw.x from the Quantum ESPRESSO package, version 7.4 [42] and the correlation-exchange functional R2SCAN [43], chosen for its balance between accuracy and computational cost. Subsequently, the band structures were calculated using SCF and NSCF with pw.x [42] and bands.x. On the other hand, the total and projected density of states (DOS) were calculated with dos.x and projwfc.x [42]. Band unfolding was performed using BandUPpy, version 0.3.4 [44], obtaining the effective band structure (EBS) of the primitive cell from the supercell. The results were processed and plotted using GNUPlot, version 5.2 [45], Origin Lab, version 9.8 [46], and Jupyter Notebooks version 7.2 [47].

Figure 12 shows the EBSs for pristine CsPbBr_3 as well as for Zn^{2+} and $\text{Zn}^{2+} + \text{I}^-$ -doped supercells. In all cases, a direct band gap at Γ is preserved, with a slight reduction from 2.20 eV to 2.18 eV, which is in agreement with previous studies on the bandgap stability in halogen- or transition-metal-doped CsPbBr_3 [48,49].

From these results, it was established that the Zn^{2+} and I^- substitutions preserve the direct semiconductor character of CsPbBr_3 , an essential condition for photovoltaic applications [48–50]. Furthermore, the band gap changes very little, thereby preserving the fundamental optical properties [49].

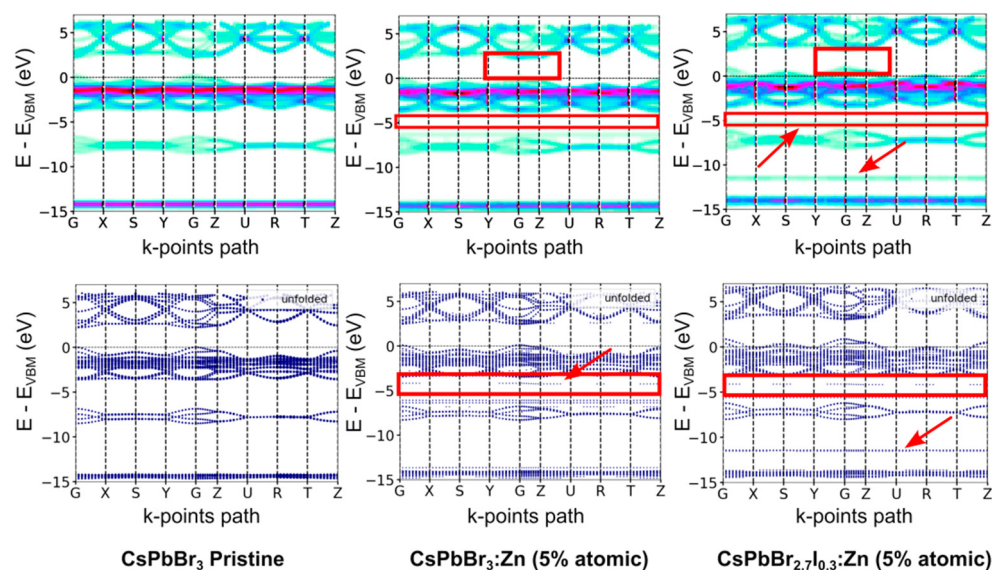


Figure 12. Effective band structures for the $\text{CsPbBr}_3\text{:Zn (5\%)}$ (center) and $\text{CsPbBr}_{2.7}\text{I}_{0.3}\text{:Zn (5\%)}$ supercells (right). The band structure for the primitive CsPbBr_3 cell is shown (left), for reference. The arrows and red boxes highlight the density-of-states contributions arising from the incorporation of Zn and I.

On the other hand, Figure 13 also displays localized states associated with the incorporation of Zn^{2+} . Based on these results, the following facts stand out:

- The shallow valence bands originate from Br 4p, with minor contributions from I 5p and Pb 6s.
- The deep valence bands include Zn 3d states (~ 7 eV), Pb 6s, I 5s, and Cs 5p.
- The conduction band is composed primarily of Pb 6p states, with minor contributions from Br 4p and Cs 6s.
- Iodine mainly affects hole transport through contributions to valence states, in agreement with prior studies on mixed-halide perovskites [50]. Zn does not introduce significant states within the band gap, suggesting that excessive Zn doping could reduce the density of available states for carrier generation, as recent studies have also noted [51].

3.5. Influence of Zn Halide Doping on the Performance of Solar Cells Fabricated with FTO/ TiO_2 / $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ /C Structure

Using as an absorber layer sequentially evaporated $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ films, carbon-based planar heterojunction PSCs of 1 cm^2 area, with a structure FTO/c- TiO_2 / $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ /carbon, were fabricated, placing special emphasis on the evaluation of the effect on the device's performance of the partial substitution of the Pb^{2+} cation by Zn^{2+} in atomic percentages that varied between 0% and 12%. The thickness of the $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ absorber layer is about 600 nm, which is similar to that of sequentially evaporated and dual-source co-evaporated CsPbBr_3 films used in the manufacture of PSCs [34,52]. c- TiO_2 films of about 40 nm-thick, prepared by RF magnetron sputtering, were used as ETL, and a carbon layer prepared from commercial carbon paste was doctor-bladed onto the perovskite absorber layer in ambient air, then dried at 120°C for 20 min and used as the device counter electrode.

In Figure 14a, the J-V curve of the best-performing device, fabricated with a $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ absorber layer, is compared with the J-V curve of the best-performing device, fabricated with a $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ film, in which the Pb^{2+} cation was replaced by Zn^{2+} at an atomic percentage of 5%. These devices were fabricated with an active area of 1 cm^2 and were reverse-recorded under illumination of 100 mW/cm^2 . The corresponding EQE spec-

trum and the dependence of PCE on annealing temperature and Zn^{2+} doping concentration are presented in Figure 14b and Figure 14c, respectively.

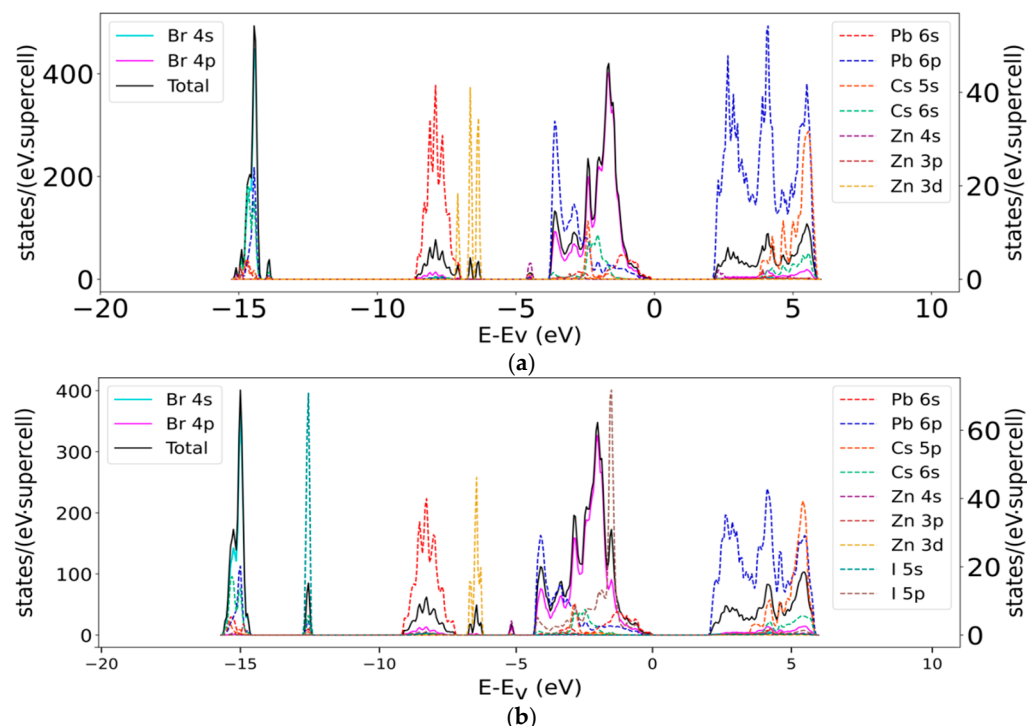


Figure 13. Density of states projected onto atomic orbitals for the 5% Zn-doped perovskite supercells: (a) $\text{CsPbBr}_3\text{:Zn}$ and (b) $\text{CsPbBr}_{2.7}\text{I}_{0.3}\text{:Zn}$. The dotted curves correspond to the right vertical axis because of their lower magnitudes.

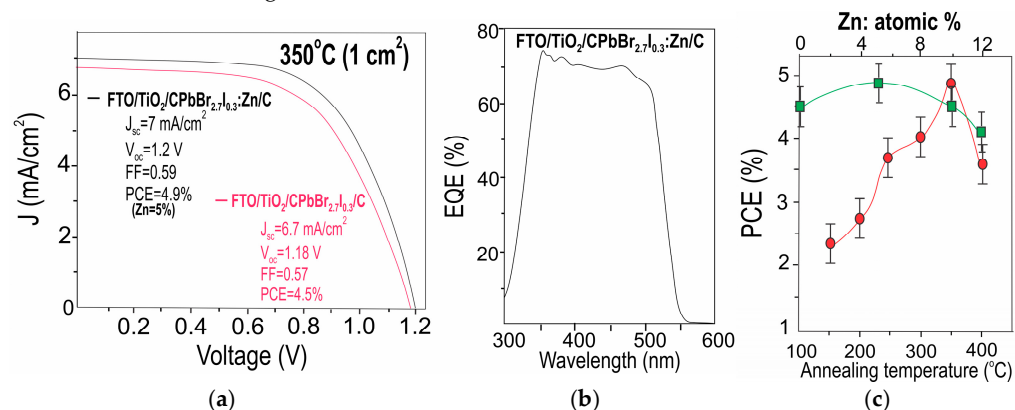


Figure 14. (a) Comparison of the J-V characteristic of the best-performing device fabricated using a 5% Zn^{2+} doped $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ absorber layer with that of a device fabricated using no doped $\text{CsPbBr}_{2.7}\text{I}_{0.3}$, (b) EQE spectra of the best Zn^{2+} -doped solar cell with area of 1 cm^2 and (c) PCE as a function of annealing temperature in air (red line) and atomic percentage of Zn^{2+} doping of $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ (green line)-based solar cells.

The 5% Zn^{2+} -doped perovskite film-based device achieved a champion PCE of 4.9%, with a J_{sc} of 7 mA/cm^2 , a V_{oc} of 1.2 V, and a FF of 0.59. On the other hand, no Zn-doped perovskite film-based device exhibited a champion PCE of 4.5%, with a J_{sc} of 6.7 mA/cm^2 , a V_{oc} of 1.18 V and a FF of 0.57.

In Figure 13b, the external quantum efficiency (EQE) of the best solar cell (5% Zn^{2+} doped) is depicted. It exhibits a high response of photons in the wavelength range 300–530 nm and a cut-off wavelength around 530 nm, in agreement with the cut-off wavelength of transmittance spectrum of the 5%-doped, absorber $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ layer

(see Figure 6a). In Figure 14c is displayed a curve of the PCE as a function of both annealing temperature in air and atomic percentage of Zn^{2+} doping of $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ -based solar cells. It is observed that device efficiency increases with annealing temperature up to 350 °C, but performance deteriorates at higher annealing temperatures. Efficiency also increases slightly upon substituting Pb^{2+} for Zn^{2+} at atomic percentages between 0% and 5%. However, it decreases sharply when the substitution of Pb^{2+} for Zn^{2+} exceeds 5%.

The results presented in Figure 14 allow us to conclude that the highest PCE values were obtained for cells manufactured using, as the absorber layer, cesium lead bromide iodide mixed perovskite thin films doped with 5% Zn^{2+} and annealed at 350 °C in air. The optimal performance of the cells fabricated under the aforementioned conditions of doping with Zn^{2+} and annealing in air is apparently attributed to the fact that the replacement of the Pb^{2+} cation by Zn^{2+} ions in inorganic $\text{CsPbBr}_{3-x}\text{I}_x$ perovskite films effectively improves both the crystallinity and morphology of this type of compounds, which lead to an improvement in the performance of the device.

4. Conclusions

In this paper, contributions were made related to the growth of thin films of cesium lead bromide iodide mixed perovskite ($\text{CsPbBr}_{3-x}\text{I}_x$), synthesized by sequential evaporation of precursors (CsBr , PbBr_2 , PbI_2). High-quality $\text{CsPbBr}_{3-x}\text{I}_x$ films were achieved by accurately tuning the thickness ratio using an electronic system that automatically controlled the deposition process via PID and PWM algorithms. A significant improvement in the morphology and crystallinity of the $\text{CsPbBr}_{3-x}\text{I}_x$ films was achieved by both post-deposition annealing at temperatures around 350 °C and Zn^{2+} halide doping. In general, samples not doped with Zn^{2+} present a morphology consisting of compact small grains, and when the Pb^{2+} cation is replaced by Zn^{2+} in small atomic percentages, the grain size increases significantly. Grain sizes around 1.33 μm can be achieved with $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ films by substituting the Pb^{2+} cation with Zn^{2+} at atomic percentages around 5%.

The influence of the partial substitution of the Pb^{2+} cation by Zn^{2+} and the Br^- anion by iodine on the band structure and density of localized states associated with CsPbBr_3 perovskites was analyzed through DFT computational calculations, using the Quantum ESPRESSO package and the correlation-exchange functional R2SCAN. From these results, it was established that the Zn^{2+} and I^- substitutions preserve the direct semiconductor character of CsPbBr_3 , with only minor variations in the band gap. The results also indicate that the conduction band is primarily composed of Pb 6p states, whereas the shallow valence bands originate primarily from Br 4p, and that the deep valence bands include Zn 3d, Pb 6s, I 5s, and Cs 5p states.

Carbon-based planar solar cells with $\text{FTO}/\text{c-TiO}_2/\text{CsPbBr}_{2.7}\text{I}_{0.3}/\text{carbon}$ structure were fabricated, and the effects of annealing temperature and Zn^{2+} doping on the quality of a reference $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ film and its photovoltaic performance were studied. The highest PCE values are obtained with cells manufactured using thin films of $\text{CsPbBr}_{2.7}\text{I}_{0.3}$ that substitute Zn^{2+} for Pb^{2+} at 5% Zn^{2+} and are annealed at 350 °C in air as the absorber layer. This result is apparently due to a significant improvement in crystallinity and morphology observed in inorganic perovskite films when they are annealed at high temperatures, and the Pb cation is substituted by Zn^{2+} ions.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

Abbreviation	Definition
NREL	National Renewable Energy Laboratory
EPFL	Swiss Federal Institute of Technology in Lausanne
PV	Photovoltaic
PSCs	Perovskite solar cells
PID	Proportional–Integral–Derivative
PWM	Pulse Width Modulation
E _g	Energy gap
EU	Urbach energy
EBS	Effective band structure
ETL	Electron transport layer
EQE	External quantum efficiency
PCE	Power conversion efficiency
XRD	X-ray diffraction
SEM	Scanning electron microscopy
DFT	Density functional theory

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