



# Article Silver-Doped CsPbI<sub>2</sub>Br Perovskite Semiconductor Thin Films

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**Abstract:** All-inorganic perovskite semiconductors have received significant interest for their potential stability over heat and humidity. However, the typical CsPbI<sub>3</sub> displays phase instability despite its desirable bandgap of ~1.73 eV. Herein, we studied the mixed halide perovskite CsPbI<sub>2</sub>Br by varying the silver doping concentration. For this purpose, we examined its bandgap tunability as a function of the silver doping by using density functional theory. Then, we studied the effect of silver on the structural and optical properties of CsPbI<sub>2</sub>Br. Resultantly, we found that 'silver doping' allowed for partial bandgap tunability from 1.91 eV to 2.05 eV, increasing the photoluminescence (PL) lifetime from 0.990 ns to 1.187 ns, and, finally, contributing to the structural stability when examining the aging effect via X-ray diffraction. Then, through the analysis of the intermolecular interactions based on the solubility parameter, we explain the solvent engineering process in relation to the solvent trapping phenomena in CsPbI<sub>2</sub>Br thin films. However, silver doping may induce a defect morphology (e.g., a pinhole) during the formation of the thin films.

Keywords: semiconductor; perovskite; silver doping; optical property; microstructure

## 1. Introduction

Metal halide perovskites (MHPs) are a next-generation semiconductor for electronics and optoelectronics, such as emerging photovoltaics (PVs), light-emitting diodes (LEDs), field-effect transistors (FETs), photodetectors, and sensors [1–5]. MHPs have a chemical formula of ABX<sub>3</sub>, in which the A-site = organic, inorganic, or hybrid (MA, FA, Cs, or mixture); the B-site = metal (Pb, Sn, or mixture); the X-site = halide (Cl, Br, I, or mixture). Here, MA and FA stand for methylammonium (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>) and formamidinium (HC(NH<sub>2</sub>)<sub>2</sub><sup>+</sup>), respectively [6,7]. In 2009, the Miyasaka group demonstrated for the first time that MAPbI<sub>3</sub> and MAPbBr<sub>3</sub> can serve as a visible-light sensitizer for PV cells, resulting in the power conversion efficiency (PCE) of 3.81% and 3.13%, respectively [8]. Then, in 2012 and 2015, MHP solar cells reached ~10% and ~20% PCE, respectively, displaying the dramatic advancement in the PV technologies for a short period of time [9,10]. Then, currently, the certified PCE of MHP solar cells was more than ~26%, indicating that perovskite PVs are on the way to commercialization by competing with the traditional silicon PVs [11–13].

In the meantime, in 2014, the Snaith group compared three materials, CsPbI<sub>3</sub>, MAPbI<sub>3</sub>, and FAPbI<sub>3</sub>, which have bandgaps ( $E_g$ ) of 1.73 eV, 1.57 eV, and 1.48 eV, respectively, and focused on the FAPbI<sub>y</sub>Br<sub>3-y</sub> (y = 0 to 1) perovskite system, demonstrating the usefulness of the slightly larger FA cation as well as the tunability of the bandgap [6]. Then, in 2015,



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). researchers paid serious attention to the fact that the organic-inorganic MHP solar cells have intrinsic stability problems, such as vulnerability in heat and humidity, originating from the presence of organic moieties such as MA and FA [14,15]. Hence, the Cahen and Hodes group compared the hybrid organic–inorganic MAPbBr<sub>3</sub> and all-inorganic CsPbBr<sub>3</sub> to demonstrate that the A-sites in the ABX<sub>3</sub> structure do not have to be organic cations for high quality PVs, which paved the way for all-inorganic MHP solar cells with enhanced stability [14]. Then, in the same year, the working all-inorganic CsPbI3 solar cells with a PCE of ~1.7–2.9% were demonstrated for the first time by kinetically overcoming the phase instability [15]. This is because, thermodynamically, the most stable phase of the CsPbI<sub>3</sub> is the non-perovskite yellow orthorhombic structure at room temperature (RT) [16]. Then, during the past decade, all-inorganic MHP solar cells were further advanced, which includes the perovskite family of CsPbI<sub>3</sub>, CsPbBr<sub>3</sub>, CsPbIBr<sub>2</sub>, and CsPbI<sub>2</sub>Br [17,18]. Among these, the two extreme materials are  $CsPbI_3$  and  $CsPbB_3$ , because the former has high visible-light absorption but poor phase stability, whereas the latter has good phase stability but low light absorption. Hence, it is imperative to find an optimum condition between these two extremes through composition engineering, bringing forth the research interests on the CsPbI<sub>2</sub>Br with the bandgap of ~1.9 eV. Here, CsPbI<sub>2</sub>Br shares the promising merits of MHPs, such as the high absorption coefficient, tunable bandgap, long exciton diffusion length, low exciton binding energy, and ambipolar transport with a high mobility, which currently results in the state-of-the-art PCE > 17% [19-21]. In addition, based on its specific wide bandgap, it can serve as a photoactive component for the top cell in the multi-junctional tandem solar cells [21].

However, CsPbI<sub>2</sub>Br also has some disadvantageous properties, such as morphological defects from fast crystallization and an un-matched energetic alignment with the charge transport layer [17,18]. Hence, many research groups have an interest in doping engineering, especially for the B-sites in the  $CsPbI_2Br$  structure [22–30]. For example, Zhu et al. reported antimony ( $Sb^{3+}$ ) doping in the B-site of  $CsPbI_2Br$ , resulting in the decrease in surface defects, the suppression of the charge recombination, and the improvement in the phase stability [22]. Ma et al. demonstrated the triple improvement in the film quality, radiative recombination, and energy-level alignment through zirconium  $(Zr^{4+})$  doping in the B-site of CsPbI<sub>2</sub>Br [23]. Han et al. reported the improved passivation, Fermi-level adjustment, and crystallinity by adding calcium (Ca<sup>2+</sup>) into CsPbI<sub>2</sub>Br [24]. In the case of Zhang et al., they doped both A- and B-sites for the air-stable  $Cs_{1-x}Rb_xPbI_2Br$  with guanidinium (GA<sup>+</sup>), leading to high crystallinity, an appropriate surface morphology, favorable electronic properties, and a reduced trap density [25]. Guo et al. proved that niobium  $(Nb^{5+})$  doping can increase the perovskite tolerance factor and stability of the  $\alpha$ -CsPbI<sub>2</sub>Br phase [26]. Yang et al. reported the air-stable  $CsPb_{1-x}Ge_xI_2Br$  (x = 0.1, 0.2, and 0.3) perovskites by germanium (Ge<sup>4+</sup>) doping, generating a better effective recombination lifetime and low trap densities [27]. Liu et al. doped CsPbI<sub>2</sub>Br by indium ( $In^{3+}$ ) and chlorine (Cl<sup>-</sup>), causing inhibition to the yellow photo-inactive phase and simultaneously improving the long-term ambient stability [28]. Duan et al. studied lanthanide (La<sup>3+</sup>, Ce<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, Yb<sup>3+</sup>, and Lu<sup>3+</sup>) doping into CsPbI<sub>2</sub>Br, producing increased grain sizes and carrier lifetimes [29]. Lau et al. carried out the less toxic strontium (Sr<sup>2+</sup>) doping into CsPbI<sub>2</sub>Br, creating the passivation effect [30]. All of these clearly demonstrate that CsPbI<sub>2</sub>Br could be an improved semiconductor by partially substituting the Pb<sup>2+</sup> sites with other metal ions for the next-generation optoelectronic devices [17,18,31].

Hence, in this study, in line with the aforementioned works [22–30], we studied the silver-doped CsPbI<sub>2</sub>Br semiconductor for the first time. Here, it is noteworthy that Chen et al. studied the silver-doped CsPbBr<sub>3</sub> semiconductor already [32]. However, in our case, we studied the more promising mixed-halide CsPbI<sub>2</sub>Br semiconductor with silver doping (theoretical) and silver bromide doping (experimental). Note that the bromine ion ( $D_N = 33.7$ ) has a higher Gutmann donor number ( $D_N$ : Lewis basicity) than the iodine ion ( $D_N = 28.9$ ) [33,34], suggesting that 'Br' can replace 'I' in CsPbI<sub>2</sub>Br with a high probability. In this work, we first calculated the silver-doping effect on the electronic structure of

CsPbI<sub>2</sub>Br using the density functional theory (DFT). Then, by adding silver bromide into the perovskite precursor solutions with a  $PbI_2/AgBr = 1:0.01-0.03$  molar ratio, we studied the doping effects on the optical, structural, and morphological properties of semiconductor thin films. In addition, we explained the solvent-trapping phenomenon during the solvent engineering process [2,35], because this trapping was detected by the infrared (IR) spectroscopy. Herein, we employed the Hildebrand and Hansen solubility parameter [36,37] to explain the intermolecular interactions between the solvent and antisolvent.

# 2. Materials and Methods

## 2.1. Materials

Lead iodide (PbI<sub>2</sub>, 99.99%, Sigma-Aldrich, Darmstadt, Germany), cesium bromide (CsBr, 99.9%, Sigma-Aldrich, Darmstadt, Germany), silver bromide (AgBr, 99.99%, AR Chemicals, Delhi, India), dimethyl sulfoxide (DMSO; 99.0%, Sigma-Aldrich), and chlorobenzene (CB, ≥99.5%, AR Chemicals, Delhi, India) were purchased and used without further purification.

# 2.2. Methods

The perovskite precursor solutions were prepared to synthesize the CsPbI<sub>2</sub>Br perovskite semiconductor without or with AgBr, for which the composition was controlled as follows:  $(CsBr)_1(PbI_2)_{1-x}(AgBr)_x$  with x = 0.00, 0.01, 0.02, and 0.03. Here, the control sample was composed of CsBr (1M) and PbI<sub>2</sub> (1M) in 1 mL DMSO. Then, after stirring at 500 rpm using a magnetic stirrer for 12 h at 70 °C, the solutions were filtered by a polytetrafluoroethylene (PTFE) syringe filter with a 0.22 µm pore size. Then, 70 µL of solution was dropped on top of the glass substrate (Microscope Slides; Grade-P.2; model number: ISO8037/IS3099 [38]; size: 76 mm × 26 mm × 1.35 mm; Rohem Instruments, Maharashtra, India) and spin-coated at 1500 rpm for 45 s using a spin coater (model: spinNXG-P2; Apex Instruments, Kolkata, India). During spinning, after ~25 s, 200 µL of CB was dispensed on top of the wet perovskite precursor film. After spin-coating, the sample was annealed thermally at 70 °C for 2 min and subsequently at 280 °C for 10 min. Then, all the characterizations were carried out under ambient conditions.

#### 2.3. Thin Film Characterizations

The X-ray diffraction (XRD) patterns were obtained using the Drawell XRD-7000 diffractometer (Shanghai, China) with Cu K $\alpha$  (3 KW) X-ray radiation ( $\lambda$  = 1.5406 Å), having a source potential of 30 kV and source current of 25 mA (here, with a  $2\theta$  range of  $10^{\circ}$ to  $60^\circ$ ; a scan rate of  $1^\circ$  per minute; a step size of  $0.01^\circ$ ). Scanning electron microscope (SEM) images were obtained using the benchtop SEM (JCM-6000 Plus, JEOL, Tokyo, Japan) at 5 kV. On the other hand, the high-resolution transmission electron microscopy (HR-TEM) images were investigated by using the model JEM-2100 (Peabody, MA, USA) at 200 kV. The absorption spectra of the film were investigated by ultraviolet–visible (UV–Vis) spectroscopy (PerkinElmer Lambda 25, Kyoto, Japan) in the wavelength range of 350 nm to 750 nm at the scanning speed of 240 nm per minute and the step size of 1 nm. The photoluminescence (PL) lifetime curves were recorded by using the time-correlated singlephoton counting (TCSPC) (model: Fluor log 3 TCSPC, Horiba, and Houston, TX, USA) with an excitation wavelength of 570 nm. The Fourier transform infrared (FT-IR) spectroscopy data were obtained using the PerkinElmer spectrum two FT-IR spectrometer (Waltham, MA, USA). Here, the attenuated total reflection (ATR) was employed to record the transmittance data from 4000 to 400 cm<sup>-1</sup> with a resolution of 0.5 cm<sup>-1</sup>. All measurements were taken at room temperature in ambient conditions.

## 2.4. Computational Method

The electronic band structures of the compounds (CsPbI<sub>2</sub>Br and Ag-doped CsPbI<sub>2</sub>Br) were calculated based on the DFT using the Vienna Ab initio Simulation Package (VASP) software (version 4.3.3) in the supercomputing resources provided by the Indian Institute of Science (Bengaluru, India).

# 3. Results and Discussion

The projector-augmented-wave (PAW) method, which is included in the VASP code, was used for all DFT calculations [39]. The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional was used for all structural relaxations [40]. After optimizing the CsPbI<sub>2</sub>Br structure based on the tetragonal  $\beta$ -CsPbI<sub>3</sub> crystal (space group P4/mbm), the lattice parameters were determined to be a = b = 6.395 Å and c = 5.988 Å. These values were very close to Chen et al.'s reports of a = b = 6.40 Å and c = 5.97 Å for the pseudo-cubic  $\alpha$ -phase CsPbI<sub>2</sub>Br [41]. Next, the 2 × 2 × 1 supercells (Figure 1) were built using the optimized structure as a basis to study the electronic structures of Cs<sub>4</sub>Pb<sub>4–x</sub>Ag<sub>x</sub>I<sub>8</sub>Br<sub>4</sub> (x = 0, 1, 2, 3, and 4) perovskites. Here, when x = 0, the structure is equivalent to four times of the pure CsPbI<sub>2</sub>Br perovskite, as shown in Figure 1a (supercell), whereas, when x = 1, 2, 3, or 4, the structures become the silver-doped perovskite, as shown in Figure 1b. Here, note that the radius of Br<sup>-</sup> is smaller than that of I<sup>-</sup>, which allows the CsPbI<sub>2</sub>Br to form a stable crystal structure compared to CsPbI<sub>3</sub>. In this study, Pb-Br and Pb-I have bond lengths of 2.9940 Å and 3.1975 Å, respectively.



**Figure 1.** (a) Unit cell and supercell of CsPbI<sub>2</sub>Br with lattice parameters,  $\mathbf{a} = \mathbf{b} = 6.395$  Å and  $\mathbf{c} = 5.988$  Å. (b) B-site substitutional doping by silver for the CsPbI<sub>2</sub>Br supercell with a size of  $2 \times 2 \times 1$ .

According to Shannon [42], the effective ionic radius at the relevant coordination number (CN) is as follows: Cs<sup>+</sup> (CN = XII) (1.88 Å), Pb<sup>2+</sup> (VI) (1.19 Å), I<sup>-</sup> (VI) (2.20 Å), and Br<sup>-</sup> (VI) (1.96 Å). Hence, if we calculate Goldschmidt's tolerance factor,  $t = (R_A + R_X) / \{\sqrt{2}(R_B + R_X)\}$ , t is 0.851 for CsPbI<sub>3</sub>, 0.855 for CsPbI<sub>2</sub>Br, and 0.862 for CsPbBr<sub>3</sub>, respectively. Here,  $R_A$ ,  $R_B$ , and  $R_X$  are the radii of A, B, and X, respectively. On the other hand, if we calculate the effective octahedral factor,  $\mu = R_B/R_X$ ,  $\mu$  is 0.541 for CsPbI<sub>3</sub>, 0.561 for CsPbI<sub>2</sub>Br, and 0.607 for CsPbBr<sub>3</sub>, respectively. Note that, for CsPbI<sub>2</sub>Br, we used the average  $\overline{R}_{I_2Br}$  =

 $(R_{I^-} \times 2 + R_{Br^-} \times 1)/3 = 2.12$  Å for the radius of the mixed halogen. Moreover, to be a cubic phase, the perovskite should have 0.81 < t < 1.11 and  $0.44 < \mu < 0.90$  [17,18].

The ionic radius of cesium is dependent on the CN. For example, if cesium has a CN of VI, VIII, IX, X, XI, and XII, the ionic radius is 1.67 Å, 1.74 Å, 1.78 Å, 1.81 Å, 1.85 Å, and 1.88 Å, respectively. Hence, if some studies in the literature adopt CN = VI instead of XII for the cesium ion, the ionic radius will be 1.67 Å. Therefore, t = 0.807 could be reported for CsPbI<sub>3</sub> and t = 0.815 for CsPbBr<sub>3</sub>, respectively [26]. However, the Cs<sup>+</sup> cation has a 12-fold coordination site (the A-site has CN = 12 for all the perovskites), not a 6-fold one [43], indicating that  $Cs^+$  (CN = XII) (1.88 Å) should be correct. Importantly, the material should have a tolerance factor of 0.9–1.0 to form an ideal cubic structure [44], indicating the aforementioned t values are somewhat away from this ideal range. In other words, they can easily undergo structural deformation for reducing the Gibbs free energy. Furthermore, thermodynamically, the most stable structure of the CsPbI<sub>3</sub> is non-perovskite orthorhombic yellow delta-phase, with  $E_g = \sim 2.82 \text{ eV}$  at the RT, whereas that of the CsPbBr<sub>3</sub> is the orthorhombic gamma-phase, with  $E_g = \sim 2.3$  eV (here, it is notable that CsPbBr<sub>3</sub> has no yellow phase) [45-47]. Therefore, it should be reasonable to study CsPbI<sub>2</sub>Br for improving the structural stability of CsPbI<sub>3</sub> via composition engineering (e.g., the B- and X-site modification in the ABX<sub>3</sub> structure) for PV applications.

Figure 2 shows (a–e) the electronic structures of the pseudo-cubic  $\alpha$ -phase Cs<sub>4</sub>Pb<sub>4–x</sub>Ag<sub>x</sub> I<sub>8</sub>Br<sub>4</sub> and (f) the resulting bandgap as a function of the silver doping level. Here, we assumed that the silver atom may stay with CsPbI<sub>2</sub>Br as a substitutional dopant according to Chen et al.'s study [32]. First, except for Cs<sub>4</sub>Pb<sub>4–x</sub>Ag<sub>x</sub>I<sub>8</sub>Br<sub>4</sub> (x = 3), all the others display the promising 'direct bandgap' characteristics. Second, although the bandgap of CsPbI<sub>2</sub>Br is known to be ~1.8–1.9 eV [48–50], the DFT results exhibit the small value, 1.361 eV, indicating the typical underestimation of the bandgap in the PBE-based DFT calculation [51,52]. Hence, we need to focus on the trend of the bandgap instead of the exact value itself. Third, when Cs<sub>4</sub>Pb<sub>4–x</sub>Ag<sub>x</sub>I<sub>8</sub>Br<sub>4</sub> (x = 2), the bandgap is the largest, 1.966 eV. Fourth, when Cs<sub>4</sub>Pb<sub>4–x</sub>Ag<sub>x</sub>I<sub>8</sub>Br<sub>4</sub> (x = 4), i.e., 4[CsAgI<sub>2</sub>Br], the bandgap is the smallest, 1.060 eV. Finally, this trend of the bandgap is summarized in Figure 2f, providing the insightful silver-doping effect on the electronic structure of CsPbI<sub>2</sub>Br qualitatively.

In our experimental study, we introduced Ag atoms into the CsPbI<sub>2</sub>Br crystals by dissolving AgBr into the perovskite precursor solutions, indicating that there should be combined effects from both Ag<sup>+</sup> cations and Br<sup>-</sup> anions because our samples are mixedhalide perovskites. Here, in the perovskite precursor solutions, Br<sup>-</sup> anions can serve as a processing additive/dopant because the bromine anions have a high Gutmann's donor number ( $D_N$  = 33.7, Lewis basicity) [33,34] affecting the crystallization of the perovskites via the modified interactions between DMSO ( $D_N$  = 29.8) and the perovskite precursors in the solution state. Figure 3 shows each optical bandgap at the onset of the absorption, for which the Tauc plot was employed for clarity (Figure 4). Here, the film thickness (1) was estimated to be ~148 nm (0% AgBr and 1% AgBr) and ~332 nm (2% AgBr and 3% AgBr), respectively. For this purpose, the following absorption coefficient ( $\alpha = -5 \times 10^4$  cm<sup>-1</sup> at 600 nm [53]) was employed:  $l = 2.302 \times Abs/\alpha$ , where 'Abs' denotes the absorbance. First of all, for the  $CsPbI_2Br$  perovskite without AgBr, the bandgap is 1.84 eV, which falls in the general bandgap ( $\sim$ 1.8–1.9 eV) of the CsPbI<sub>2</sub>Br perovskite [48–50]. Here, it is notable that CsPbI<sub>3</sub> and CsPbBr<sub>3</sub> have the bandgaps of ~1.73 eV and ~2.3 eV, respectively. However, when AgBr was employed into the perovskite precursor solutions, the resulting bandgap increased slightly from 1.87 eV (at 1% AgBr) to 1.95 eV (at 2% AgBr) and 1.96 eV (at 3% AgBr). Figure 3b shows the summary of the results, i.e., the bandgap as a function of the AgBr doping concentrations. It is worthy to remind that the bandgap is a key factor in the 'stability and cost' for practical solar cells, determining the theoretical PCE based on the Shockley–Queisser limit [54]. Importantly, Ravi et al. pointed out that, in CsPbX<sub>3</sub> perovskite, the conduction band minimum (CBM) is dominantly affected by Pb 6p orbitals, whereas the valence band maximum (VBM) is mainly determined by anti-bonding hybridization Pb 6s and X np orbitals, specifically, the major effect from X np [55]. Therefore, the bandgap shift in Figure 4 could be explained as follows. Ag-doping may affect the CBM shift, whereas Br codoping may contribute to the VBM move. However, these effects will be very small because of the slight AgBr doping concentration of ~1–3%. Then, we measured the PL lifetime for the CsPbI<sub>2</sub>Br when AgBr was 0, 1, 2, and 3%. Accordingly, as shown in Figure 5, the PL lifetime was enhanced from 0.990 ns (at 0% AgBr) to 1.187 ns (at 3% AgBr) with increasing AgBr amounts, suggesting that the AgBr doping helps minimize the nonradiative transition according to the literature reports [22–30,32].



**Figure 2.** Band structure of the pseudo-cubic  $\alpha$ -phase Cs<sub>4</sub>Pb<sub>4-x</sub>Ag<sub>x</sub>I<sub>8</sub>Br<sub>4</sub> when (**a**) x = 0, (**b**) x = 1, (**c**) x = 2, (**d**) x = 3, and (**e**) x = 4. (**f**) Bandgap as a function of x in Cs<sub>4</sub>Pb<sub>4-x</sub>Ag<sub>x</sub>I<sub>8</sub>Br<sub>4</sub>.



**Figure 3.** (a) UV–Vis spectra of CsPbI<sub>2</sub>Br as a function of the AgBr concentration. (b) Bandgap as a function of the AgBr doping concentration (%). Optical bandgap determination for CsPbI<sub>2</sub>Br as a function of the AgBr concentration by the Tauc plot.



**Figure 4.** Optical bandgap determination for CsPbI2Br as a function of the AgBr concentration (**a**) 0%, (**b**) 1%, (**c**) 2% and (**d**) 3% by the Tauc plot. Here, each arrow indicates the tangent line for determining the optical bandgap.



Figure 5. PL lifetime of the CsPbI<sub>2</sub>Br thin film as a function of the AgBr concentration.

The FT-IR spectra were characterized for the CsPbI<sub>2</sub>Br thin film as a function of the AgBr doping in the perovskite precursor solutions. As shown in Figure 6a, we can find only the FT-IR peaks from the solvents remaining inside of the CsPbI<sub>2</sub>Br thin film. This observation indicates that the trace amounts of the solvent molecules may survive in the trapped state inside of the perovskite film, although the annealing temperature (>250 °C) was higher than the boiling points of each solvent molecules (DMSO: 189 °C and CB: 132 °C; their structures are given in Figure 6b). Here, the detailed peak assignment is as follows [56]: First, in the high frequency regions, 3025–2849 cm<sup>-1</sup>, =C-H and –C-H vibrations were observed from the DMSO and CB molecules inside of the CsPbI<sub>2</sub>Br crystals. At 1676 cm<sup>-1</sup>, a -C=C vibration from the aromatic ring of CB was detected. On the other hand, at 1387 cm<sup>-1</sup>, 1092 cm<sup>-1</sup>, and 738 cm<sup>-1</sup>, -CH<sub>3</sub>, S=O, and –C-Cl vibrations were displayed, respectively. Finally, the small peak at 463 cm<sup>-1</sup> is ascribed to the molecular vibration of the antisolvent CB.

Importantly, Figure 6c shows the solvent engineering process [35] to explain the solvent trapping phenomena detected via the FT-IR. Here, the solvent engineering procedure is as follows. The antisolvent (chlorobenzene) dripping on top of the wet perovskite precursor film (solvent: DMSO) during spinning brings forth the fast crystallization and deposition of a perovskite film. Here, to understand the intermolecular interactions, the solubility parameter ( $\delta$ ) data [36] of the solvent, antisolvent, and perovskite are required. First, DMSO and CB have  $\delta = 14.5 \text{ (cal/cm}^3)^2$  and  $\delta = 9.5 \text{ (cal/cm}^3)^2$ , respectively [57]. In the case of CsPbI<sub>2</sub>Br, we may estimate it from the water contact angle ( $\theta_c = 32.76^\circ$ ) data reported by Chen and coworkers [58]. Li and Neumann [59] suggested the relation between the contact angle and surface energy,  $\cos \theta_c = -1 + 2\sqrt{\gamma_{sv}/\gamma_{lv}} \cdot \exp\left[-\overline{\beta}(\gamma_{lv} - \gamma_{sv})^2\right]$ , where  $\gamma_{lv}$ ,  $\gamma_{sv}$ , and  $\gamma_{sl}$  are the surface energies for liquid–vapor, solid–vapor, and solid–liquid, respectively. The constant  $\overline{\beta}$  is 0.000115 m<sup>4</sup>/mJ<sup>2</sup> and  $\gamma_{lv}$  is 72.8 mJ/m<sup>2</sup> for water, respectively. Then, by inputting  $\theta_c = 32.76^\circ$  into the aforementioned Li–Neumann's equation, we may estimate  $\gamma_{sv} = 63.05 \text{ mJ/m}^2$ . Then, from the relation of  $\delta \left[ (\text{cal/cm}^3)^2 \right] = 1.829058 \sqrt{\gamma_{sv}}$  [60–62], we obtained  $\delta = 14.5 \text{ (cal/cm}^3)^2 \text{ or } \delta'(\text{SI unit}) = \delta \times 2.0455 = 29.7 \text{ MPa}^{1/2}$ , respectively (Table 1). Hence, because CsPbI<sub>2</sub>Br and DMSO have (almost) the same solubility parameter, there is high probability that DMSO may be trapped in the CsPbI<sub>2</sub>Br. However, for the case of CB, the 'solvent-antisolvent' (DMSO and CB) molecules are miscible because of the entropy-driven mixing, affording CB to wash and remove the DMSO molecules during its dripping process [35]. However, when CB was dropped on top of the wet perovskite

precursor film, CB could also be trapped into the crystal structure of CsPbI<sub>2</sub>Br, although CB and CsPbI<sub>2</sub>Br have two different polarities, i.e., CB is slightly polar (polarity index = 2.7) but CsPbI<sub>2</sub>Br and DMSO (polarity index = 7.2) are highly polar [63]. Hence, CB's trapping could be understood based on the physical trap instead of the chemical affinity between the CB and the CsPbI<sub>2</sub>Br perovskite. On the other hand, DMSO can be trapped for two reasons, i.e., affinity and physical confinement. Accordingly, even after thermal annealing at 280° for 10 min, trace amounts of the solvents could be trapped, as demonstrated in the FT-IR spectra in Figure 6a.



**Figure 6.** (a) FT-IR spectra of  $CsPbI_2Br$  with or without AgBr when processed with dimethyl sulfoxide (DMSO) and chlorobenzene (CB). (b) Chemical structures of DMSO and CB. (c) Solvent engineering process: when CB is dripping on top of the wet perovskite (precursor) film, DMSO can be washed away. During this process, some solvent molecules could be trapped in the perovskite thin film.

**Table 1.** Solubility parameter, molecular weight, density, and molar volume of solvent, non-solvent, and CsPbI<sub>2</sub>Br.  $\delta$  (SI unit) =  $\delta \times 2.0455$ .

Chemical	$\delta^{'}$ (MPa <sup>1/2</sup> )	$\delta$ [(cal/cm <sup>3</sup> ) <sup>2</sup> ]	MW (g/mol)	ho (g/cm <sup>3</sup> )	$\hat{V}_i$ (cm <sup>3</sup> /mol)
DMSO	29.7	14.5	78.13	1.10	71.03
CB	19.4	9.5	112.56	1.11	101.41
$CsPbI_2Br$	29.7	14.5	673.82	4.79 <sup>a</sup>	140.67

<sup>a</sup> This is estimated based on the lattice parameters,  $\mathbf{a} = \mathbf{b} = 0.640$  nm and  $\mathbf{c} = 0.597$  nm.

Figure 7a shows the XRD patterns of CsPbI<sub>2</sub>Br as a function of the AgBr doping concentration. First, in the absence of AgBr, the CsPbI<sub>2</sub>Br perovskite thin film displays the typical (100) and (200) peaks [64]. However, by increasing the AgBr concentration (see ~2–3% AgBr), the other peaks such as (211), (300), and (222) are intensified, indicating that the crystallographic ordering decreases with the increasing AgBr concentrations. This observation implies that the crystallization kinetics were changed when the AgBr was introduced into the perovskite precursor solutions. Second, we estimated the crystallite size (*D*) by using Scherrer's relation of  $D = 0.9\lambda/(B \cdot \cos \theta)$ , where  $\lambda$  (=0.154 nm) is the wavelength of the X-ray, whereas *B* is the full width at half-maximum (FWHM) at the diffraction angle of  $\theta$ . The results are summarized in Figure 7b and Table 2. As shown in Figure 7b, there was no clear linear trend when AgBr was introduced into the perovskite precursor, implying that, although the morphology might be changed through different crystallization kinetics, the crystallite size (i.e., the average single crystalline domains in the polycrystalline structure) were not much changed, but rather similar to all the conditions, whether doped or not.



**Figure 7.** CsPbI<sub>2</sub>Br as a function of AgBr doping: (**a**) XRD patterns and (**b**) crystallite size. The PDF reference card number is 80-4039 [65,66].

Plane	AgBr (%)	2θ (°)	B (rad)	D (nm)
	0	15	0.003036	46.1
(100)	1	15	0.003601	38.8
(100)	2	15	0.003334	41.9
	3	15	0.003573	39.1
	0	30	0.003640	45.4
(200)	1	30	0.004319	33.2
(200)	2	30	0.003140	45.7
	3	30	0.004347	33.0

Table 2. Crystallite size in CsPbI<sub>2</sub>Br as a function of the AgBr doping concentration.

Figure 8a,b show the stability test of the perovskite thin film: (a) CsPbI<sub>2</sub>Br without AgBr and (b) CsPbI<sub>2</sub>Br with 1% AgBr doping. These two samples were selected for this test because the surface morphologies were relatively uniform compared to the others (~2–3% AgBr-doped perovskite samples). Interestingly, both samples show the growth of the minor peaks at the (211) and (222) crystallographic planes with time, indicating that the orientational ordering decreases with time. Here, it is notable that, except for single crystalline perovskite thin films, all the polycrystalline films are thermodynamically metastable because the defect area (including polycrystalline nature) makes the surface

energy increase. Hence, for the lowering of the Gibbs free energy, the sample can undergo phase transition. In this case, by decreasing the orientational order (i.e., increasing the (211)-(222) XRD peaks), the film may reduce its free energy. When we see the CsPbI<sub>2</sub>Br sample without the AgBr doping in Figure 8a, compared to the same sample (but different batch) in Figure 7 (black solid line), the additional strong peak at the (300) crystallographic plane was observed [i.e., a more orientational order because the (100), (200), and (300) planes are equivalent], indicating the batch-to-batch partial uncertainty depending on the drying process in the laboratory under ambient conditions. Importantly, the 1% AgBr-doped CsPbI<sub>2</sub>Br shows the structural stability (i.e., the XRD peak position is the same with aging time), but the 0% AgBr sample clearly shows the major peak's shift to the left direction (i.e., a partial expansion of crystal; see the dotted red line box in Figure 8a). This aging effect data proves that the AgBr doping should contribute to the structural stability of the CsPbI<sub>2</sub>Br perovskite films. The results are reasonable because the AgBr addition increases the stability (a wider bandgap and improved tolerance to the environments).



Figure 8. Structural stability test by the XRD: (a) CsPbI<sub>2</sub>Br without AgBr and (b) CsPbI<sub>2</sub>Br with 1% AgBr.

Figure 9 shows the SEM images displaying the microstructural morphologies of the CsPbI<sub>2</sub>Br sample as a function of the AgBr doping concentration. First, the CsPbI<sub>2</sub>Br thin films (a) without the AgBr and (b) with the 1% AgBr are relatively uniform, whereas the other films with the ~2–3% AgBr are nonuniform, displaying the crystal domains and defect sites clearly. Probably, the samples (c and d) were grown very fast in the presence of high doping (~2–3% AgBr). However, it is worth reminding that, according to the XRD data in Figure 7, the crystallite size (the average single-crystalline domains) is not much different from sample-to-sample. The average crystallite size is  $41.5 \pm 3.4$  nm and  $39.3 \pm 7.2$  nm at the (100) and (200) crystallographic planes, respectively. However, as shown in Figure 9, the film processing condition should be optimized further for photonic devices, which will be included in our future work. Finally, we note that, without annealing (>250 °C), the CsPbI<sub>2</sub>Br sample shows phase impurities at room temperature due to polymorphism (see Table S1 and Figure S1 in Supplementary Materials).



**Figure 9.** SEM images: (**a**) CsPbI<sub>2</sub>Br without AgBr, (**b**) CsPbI<sub>2</sub>Br with the 1% AgBr (**c**) CsPbI<sub>2</sub>Br with the 2% AgBr, and (**d**) CsPbI<sub>2</sub>Br with the 3% AgBr.

# 4. Conclusions

CsPbI<sub>2</sub>Br is an interesting light-harvesting next-generation semiconductor by positioning between CsPbI<sub>3</sub> (with a low stability but high absorption) and CsPbBr<sub>3</sub> (with a high stability but low absorption), displaying the bandgap of ~1.84–1.96 eV and improved stability compared to CsPbI<sub>3</sub>. First, we demonstrated the tunability of the CsPbI<sub>2</sub>Br bandgap by substituting Pb with Ag through the DTF calculation. Herein, the bandgap reached the maximum when Pb/Ag = 50:50% (i.e., x = 2 in  $Cs_4Pb_{4-x}Ag_xI_8Br_4$ ). Second, when we added AgBr into the perovskite precursor solution from 1% to 3%, the bandgap increased from ~1.87 eV to ~1.96 eV, which is qualitatively in line with the DFT prediction. Third, the PL lifetime was enhanced by employing AgBr into the perovskite precursor solution. Fourth, the FT-IR spectra exhibited that the solvent/antisolvent molecules were trapped inside of the perovskite thin films. Fifth, when AgBr was introduced (or the aging time was increased), the minor XRD peaks at the (211) and (222) crystallographic planes were partially enhanced, indicating the diminished orientational ordering in the film. Sixth, when AgBr was incorporated into the perovskite film (with a thickness of ~148–332 nm), the crystallization kinetics were changed, affecting the morphologies of the films. Seventh, based on the XRD data, AgBr doping was observed to contribute to the enhanced stability of the CsPbI<sub>2</sub>Br perovskite structure. Finally, it should be valuable to study further allinorganic CsPbI<sub>2</sub>Br materials for the development of perovskite solar cells with enhanced stability as our future works.

**Supplementary Materials:** The following supporting information [16,43] can be downloaded at: https: //www.mdpi.com/article/10.3390/electronicmat5020005/s1, Table S1: Analysis of the selected area electron diffraction (SAED) image for CsPbI<sub>2</sub>Br without annealing at room temperature. Figure S1: HR-TEM image of  $CsPbI_2Br$  with different scale bars: (a) 2 nm, (b) 5 nm, and (c) 10 nm. (d) SAED pattern of  $CsPbI_2Br$  displaying the phase impurity at room temperature.

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**Data Availability Statement:** The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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