Elucidating the Factors Limiting the Photovoltaic Performance of Mixed Sb–Bi Halide Elpasolite Absorbers

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Although Cs₂AgBiBr₆ halide elpasolites have gained substantial attention as potential nontoxic and stable alternatives to lead–halide perovskites, they are limited by their wide bandgaps (>2.2 eV). Alloying with Sb into the pnictogen site has been shown to be an effective method to lower the bandgap, but this has not translated into improvements in photovoltaic (PV) performance. Herein, the underlying causes are investigated. Pinhole-free films of Cs₂Ag(SbₓBi₇₋ₓ)Br₆ are achieved through antisolvent dripping, but PV devices still exhibit a reduction in power conversion efficiency from 0.44% ± 0.02% (without Sb) to 0.073% ± 0.007% (90% Sb; lowest bandgap). There is a 0.7 V reduction in the open-circuit voltage, which correlates with the appearance of a sub-bandgap state ~0.7 eV below the optical bandgap in the Sb-containing elpasolite films, as found in both absorbance and photoluminescence measurements. Through detailed Williamson–Hall analysis, it is found that adding Sb into the elpasolite films leads to an increase in film strain. This strain is relieved through aerosol-assisted solvent treatment, which reduces both the sub-bandgap state density and energetic disorder in the films, as well as reducing the fast early decay in the photogenerated carrier population due to trap filling. This work shows that Sb alloying leads to the introduction of extra sub-bandgap states that limit the PV performance, but can be mitigated through post-annealing treatment to reduce disorder and strain.

1. Introduction

Halide elpasolites (also referred to as double perovskites) have gained substantial attention over the past few years because they are structurally analogous to the lead–halide perovskites, but are free from toxic regulated elements, and are structurally stable in ambient air. The most popular of these elpasolites for optoelectronics is Cs₂AgBiBr₆, which has been found to have low charge-carrier lifetimes exceeding 100 ns (in thin films), although recent studies have suggested that this is due to the detrimental formation of small polarons. Apart from questions around charge-carrier transport, an important limitation with Cs₂AgBiBr₆ is that its bandgap (2.25 eV) exceeds the optimal values for single-junction photovoltaics (PVs), indoor PVs, as well as top-cells for tandem PVs. Partly because of the wide, indirect bandgap, attempts at fabricating single-junction PVs have yielded power conversion efficiencies (PCEs) up to only 4.23%, with most reports <3%. Indeed, there is still much variation in the PCEs reported for Cs₂AgBiBr₆ solar cells between different groups, suggesting that not all parameters influencing performance have yet been uncovered or are yet well controlled.

While reductions in the bandgap of Cs₂AgBiBr₆ could be achieved by exchanging the bromide for iodide, Cs₂AgBiI₆ is unstable against decomposition and therefore challenging to synthesize. A very recent study showed that a promising route to enhancing light absorption is through hydrogenation of Cs₂AgBiBr₆, and this led to solar cells with a stabilized power output efficiency of 6.25%. Another alternative that has been considered by several groups is to alloy Sb into the pnictogen site, which leads to bandgap bowing, such that the lowest bandgap (of 2.08 eV in thin films) is achieved with...
Cs$_2$AgSb$_{0.9}$Bi$_{0.1}$Br$_{6}$, rather than Cs$_2$AgSbBr$_6$. Smaller bandgaps have been reported in bulk powders and single crystals, with values as low as 1.55 eV reported. Preliminary attempts have been made to investigate whether these reductions in bandgap could be translated into improvements in PV performance. However, groups have thus far reported that Sb alloying leads to a reduction in the PCE from >1% for Cs$_2$AgBiBr$_6$ down to <0.3% for alloyed Sb-Bi elpasolite absorbers. In particular, across multiple reports, it has been found that instead of improving the short-circuit current density ($J_{SC}$), introducing Sb into Cs$_2$AgBiBr$_6$ results in reductions in $J_{SC}$, and with open-circuit voltages ($V_{OC}$) well below $E_g/q$ (losses exceeding 1.4 V), where $E_g$ is the optical bandgap and $q$ the elementary charge.

Herein, we investigate the factors behind the reduction in PV performance when alloying Sb into Cs$_2$AgBiBr$_6$. To determine whether these reductions in performance are due to shunting effects, we developed an antisolvent dripping method to tune the morphology of the Cs$_2$AgSb$_{0.9}$Bi$_{0.1}$Br$_6$ films. The bulk properties of these films were analyzed using detailed photoluminescence (PL) and absorbance (via photothermal deflection spectroscopy, or PDS) measurements, from which it was found that sub-bandgap states were introduced through Sb alloying that the morphology was comprised of interconnected grains (rather than an island-like microstructure), albeit with small pinholes forming at some grain boundaries (Figure 1c). When complete PV devices were fabricated (device structure: FTO/TiO$_2$/mesoporous TiO$_2$/Cs$_2$AgSb$_{0.9}$Bi$_{0.1}$Br$_6$/PTAA/Au, see Section 4), rectification was still obtained from Cs$_2$AgBiBr$_6$, with a fill factor (FF) of 58% ± 3% (Table 1). However, for Cs$_2$AgSbBr$_6$ and Cs$_2$AgSb$_{0.9}$Bi$_{0.1}$Br$_6$, the FFs were 50% or below, and the PCEs of the devices were below 0.1% (Table 1).

To ensure that shunting due to pinholes in the Sb-containing elpasolite films did not limit PV performance, we investigated the use of antisolvent dripping to improve film morphology. This approach has been widely used in spin-coated lead–halide perovskites to achieve films without pinholes. In this method, an antisolvent with low solubility for the double perovskite or inorganic-solvent complex intermediates is dropped onto the solution-processed films, and analyzed the effects on the density of sub-gap states and charge-carrier lifetime.

2. Results and Discussion

2.1. Photovoltaic Performance

Thin films were initially deposited by solution processing, following our previously reported approach. However, the film morphology was found to be noncontinuous, with many large pinholes, especially in the films containing Sb (Figure 1a,b, and S1, Supporting Information). The mesoporous TiO$_2$ scaffold that the films were deposited onto was visible between the grains of the Sb-containing elpasolites, which formed an island-like morphology (Figure 1a,b). Cs$_2$AgBiBr$_6$ had a much smaller density of pinholes, and the morphology was comprised of interconnected grains (rather than an island-like microstructure), albeit with small pinholes forming at some grain boundaries (Figure 1c).

![Figure 1. Scanning electron micrographs of: a,d) Cs$_2$AgSbBr$_6$, b,e) Cs$_2$Ag(Sb$_{0.9}$Bi$_{0.1}$)Br$_6$, and c,f) Cs$_2$AgBiBr$_6$ thin films deposited onto glass/FTO/compact TiO$_2$/mesoporous TiO$_2$ substrates. The films were prepared (a–c) without and (d–f) with toluene antisolvent dripping during growth.](image)
the spinning film. This washes away the original solvent (dimethyl sulfoxide, or DMSO), inducing rapid supersaturation. As a result, a high density of nuclei is formed, which improves the likelihood of the microstructure being free from pinholes. We compared the commonly used low-polarity antisolvents used with polar inorganic compounds (toluene, chlorobenzene, and chloroform), as well as ethanol (in which we found Cs₂AgBiBr₆ to have low solubility). From these, we found that toluene was the most effective (see Section 4 for details on the processing). In the cases of Cs₂AgSbBr₆ and Cs₂AgSb₀.₉Bi₀.₁Br₆ shown in Figure 1, it can be seen that the morphology changed from island-like (no antisolvent) to continuous (with toluene antisolvent), thus eliminating pinholes from the areas analyzed. However, the use of toluene antisolvent for Cs₂AgBiBr₆ led to no improvements in film morphology (Figure 1c,f). Therefore, for Cs₂AgBiBr₆ PVs, we used absorber layers deposited without antisolvent treatment.

Despite the improvements in film morphology, the PV devices based on Sb-containing films did not improve in PCE following antisolvent treatment (Table 1). Indeed, the PCE remained an order of magnitude lower than that of Cs₂AgBiBr₆ PVs, despite the antisolvent-treated Sb-containing films having fewer pinholes. This suggests that the differences in PV performance may be related to properties of the bulk of the materials, rather than differences in morphology.

Examining the PV performance shown in Figure 2 in detail, it is noteworthy that the PV devices based on Cs₂AgSb₀.₉Bi₀.₁Br₆ had \( V_{OC} \approx 0.7 \) V below the \( V_{OC} \) of Cs₂AgBiBr₆ PVs (Figure 2a, Table 1). This substantial reduction in \( V_{OC} \) is consistent with increases in the reverse-bias dark current density by over an order of magnitude at \(-0.2 \) V applied bias with the addition of Sb (Figure 2b). These results suggest that loss channels are introduced to the devices with Sb-containing films. Note that the dark currents could not be measured at reverse biases beyond \(-0.2 \) V owing to diode breakdown.

Furthermore, in increasing the Sb content of the elpasolite films from 0% to 90% and 100%, there was a monotonic decrease in the \( J_{SC} \) (Figure 2a, Table 1), which is consistent with increased nonradiative recombination. The trends in \( J_{SC} \) were also consistent with those of the external quantum efficiency (EQE) measurements, in which EQE values decreased with increasing Sb content (Figure 2c). The integrated \( J_{SC} \) from EQE measurements were 0.87 (100% Bi), 0.22 (90% Sb), and 0.03 mA cm\(^{-2}\) (100% Sb), which are close to the measured \( J_{SC} \) values shown in Table 1.

It is notable that the EQE curve for the Cs₂AgBiBr₆ PV device exhibited a clear peak centered at 2.8 eV (Figure 2c), which is consistent with the sharp peak in the optical absorption spectrum (see Ref. [14]) that has been attributed to the concentrated states in the conduction band, as well as excitonic features.[14,32] With increasing Sb content, this peak in the EQE spectrum becomes less pronounced (Figure 2c), in agreement with our previous measurements of the absorption spectra of the films, in which these sharp features become obscured due to the broadening arising from increased disorder in the films.[14] In plotting the EQE spectra on a log-linear scale (Figure 2d), we can more clearly observe the onset of EQE. From these plots, we can see that the PVs based on films containing 90% Sb had the lowest onset, which

![Figure 2. Photovoltaic performance of Cs₂AgSbₓBi₁₋ₓBr₆ thin films. a) Current density (J) versus voltage (V) curves measured under 1 sun illumination (filled: forward sweep, open: reverse sweep), b) J–V curves measured in the dark (reverse sweep only). A comparison of the forward and reverse sweeps of the dark J–V curves are shown in Figure S2, Supporting Information. c) External quantum efficiency (EQE) of the photovoltaic devices and d) log-linear plot of the EQE spectrum. Note: the 100% Bi sample was not antisolvent treated, whilst the Sb-containing samples were to compare films with the best morphology.](image-url)
is in agreement with these materials having the smallest optical bandgap. However, despite the reductions in the optical bandgap, there was no improvement in performance due to the loss channels introduced with Sb alloying, as well as the low absorption coefficients near the indirect bandgaps of these materials. These results all together suggest that the performance of Sb-containing elpasolites is limited by the bulk properties, rather than the morphology. Therefore, in subsequent sections, we analyze the optical and structural properties of the bulk in detail, focusing consistently on films prepared without antisolvent treatment.

2.2. Optical Loss Characterization

To understand the cause of the loss channels introduced to the PV devices through the addition of Sb into the elpasolite films, we measured the sub-bandgap absorbance through photothermal deflection spectroscopy (PDS; Figure 3a), as well as the photoluminescence (PL) spectra of the bare films (Figure 3b). From the PDS spectra, it can be seen that as the Sb content of the bare elpasolite films increased, there was a concomitant increase in the sub-bandgap absorbance, which originates at \( \approx 1.55 \text{ eV} \). These measurements are consistent with the PL spectra, which showed that alloying Sb into Cs2AgBiBr6 led to the PL peak (originally centered at 1.94 eV) being substantially quenched and red-shifted to a broad peak centered at approximately between 1.5 and 1.55 eV (Figure 3b). These results all suggest that Sb-alloying leads to a sub-bandgap state being introduced that acts as a loss channel. Photogenerated charge carriers relax to this state, from which they weakly luminesce. These results agree with previous observations that Sb addition into Cs2AgBiBr6 quenches the PL. In addition, the sub-bandgap state located at 1.55 eV is 0.7 eV below the optical bandgap of Cs2AgBiBr6 (2.25 eV), which matches the 0.7 V loss in \( V_{OC} \) in the PV devices. That is, adding Sb into Cs2AgBiBr6 would lower the \( V_{OC} \) not only due to a reduction in bandgap (from 2.25 to 2.08 eV with 90% Sb) or increases in Urbach energy, but would also be substantially reduced by charge-carriers relaxing to the sub-bandgap state introduced (illustrated in Figure S3, Supporting Information).

2.3. Aerosol-Assisted Post-Annealing Treatment

We next investigated whether the density of sub-bandgap states in the Sb-containing elpasolites could be reduced through an aerosol-assisted post-annealing treatment. The aerosol treatment involves annealing thin films in a solvent-vapor-rich environment, created by flowing an aerosol of the solvent over the films at an optimized temperature and flow rate. The solvent vapors are insufficient for dissolving the thin film, but enable mass transport between grains, in which lower energy large grains grow at the expense of higher energy small grains. This Ostwald ripening process leads to the formation of larger grains, with improved crystallinity and uniformity in grain size, as well as reduced tensile strain in thin films. Aerosol annealing with lead–halide perovskites has been demonstrated to give rise to reduced nonradiative recombination, improved optoelectronic uniformity between grains, as well as improved performance in PVs and photodetectors.

To investigate the effect of aerosol annealing on the bulk optical and structural properties of the halide elpasolites, we again prepared films without antisolvent treatment. We used a 50:50 mixture of N,N-dimethylformamide (DMF) and DMSO for the aerosol, and annealed the films at temperatures from 100 to 150 °C for 5 min during the treatment. Following aerosol annealing, the films were annealed again at 150 °C in an inert N2 environment (see Section 4). We focused on the 90% Sb alloy films because these are the lowest bandgap materials, and found that the optical bandgap (2.03 eV) and phase purity remained unchanged following aerosol annealing (Figure S5 and S6, Supporting Information, respectively). From PDS measurements, we found that the sub-bandgap absorbance decreased following aerosol annealing (Figure 4a), with the integrated area of the sub-bandgap absorbance monotonically reducing as the annealing temperature increased (Figure 4b). In particular, there was a steady decrease in the absorption onset at 1.55 eV as the aerosol annealing temperature increased (Figure 4a), suggesting...
a decrease in the density of this sub-bandgap state. In addition, the Urbach energy reduced from 120 (pristine) to 94 meV (aerosol) annealed at 150 °C (Figure 4b), showing that aerosol annealing also reduced energetic disorder in these materials.

We analyzed the X-ray diffraction (XRD) patterns to understand the structural changes occurring following aerosol annealing. By profile fitting the XRD patterns (Figure S6, Supporting Information), we obtained the full width at half maximum (FWHM) of the main diffraction peaks, and how they vary with the aerosol annealing temperature (see Figure S6, Supporting Information for diffraction patterns). This may be due to Sb3⁺ having a smaller ionic radius (90 pm) than Bi3⁺ (117 pm) when octahedrally coordinated,[37] such that introducing Sb to the pnictogen site may have caused local contractions of the lattice, and hence local strain. These grains likely have higher energy, and aerosol annealing would then result in lower strain grains growing in the expense of higher strain, higher energy grains, thus leading to the reduction in film strain and defect density found.

Finally, we determined how aerosol annealing influenced the charge-carrier kinetics of the Cs₂AgSb₀.₉Bi₀.₁Br₆ films. For this,
we used transient absorption (TA) spectroscopy, which measures the change in absorbance of the films following photoexcitation with a pulsed pump laser (355 nm wavelength). A positive relative change in transmittance ($\Delta T/T$) is due to photoexcited charge carriers occupying an empty state that existed before excitation (e.g., electrons in the conduction band), and this is the ground state bleach (GSB). From Figure 5a,c, it can be seen that the onset in GSB was at just below 600 nm wavelength (2.06 eV), in agreement with the measured optical bandgap of these materials (2.03 eV, Figure S5, Supporting Information). Photoinduced absorption (PIA) features are absent from these TA spectra, in contrast to Cs$_2$AgBiBr$_6$,[38] and this allowed us to more clearly monitor the decay in the photo-excited carrier population. We integrated over 420–560 nm wavelength and measured the GSB kinetics (Figure 5b,d). At a low excitation fluence of 53 $\mu$J cm$^{-2}$ pulse$^{-1}$, the pristine sample decayed faster than the aerosol-annealed samples over the first 100 ns (Figure 5b). By contrast, under a high fluence of 93 $\mu$J cm$^{-2}$ pulse$^{-1}$, the pristine sample decayed in a comparable manner to the other samples (Figure 5d). Note that both laser fluences used exceed that which would produce the same excess carrier density as 1 sun illumination (see Note S1, Supporting Information).

These TA results are consistent with the pristine sample having a high sub-bandgap trap density. It is possible that under low fluence, the photoexcited carrier population rapidly relaxed to this sub-bandgap state, resulting in a depopulation of carriers in the conduction or valence bands. Indeed, in comparing the GSB spectra at a pump-probe delay of 5 ns (Figure 5a), it can be seen that the pristine sample had the lowest $\Delta T/T$ intensity, which is consistent with carrier depopulation. The sample aerosol annealed at 100 °C had the next lowest $\Delta T/T$ intensity, whereas the samples annealed at 125 and 150 °C had the highest intensities and were similar (Figure 5a). This is consistent with a steady reduction in sub-bandgap state density with increasing aerosol annealing temperature.

With an increase in excitation fluence, the pristine sample exhibited a marked increase in $\Delta T/T$ intensity (Figure 5c), especially at the low-energy edge. This is consistent with the sub-bandgap state being filled under high fluence, such that there was a slower depopulation of the excited state. We fit the GSB kinetics with a phenomenological biexponential model to numerically describe these decays to enable a quantitative comparison, and the fitted parameters are shown in Table 2. From these fits, we found a marked increase in the effective lifetime of the pristine sample when increasing the fluence (Table 2; see also Figure S11, Supporting Information), which is consistent with the earlier explanation made. But we also found that the samples aerosol annealed at the higher two temperatures...
of 125 and 150 °C also increased in lifetime with increasing fluence (Table 2 and Figure S11, Supporting Information), albeit with smaller differences than in the pristine sample. This was consistent with these samples also exhibiting higher ΔT/T intensities as the fluence increased, particularly at the low-energy edge (Figure S5a vs c). These results suggest that the sub-bandgap states in the materials aerosol annealed at higher temperatures were not eliminated, and that these materials still underwent a degree of carrier depopulation to the sub-bandgap states under low fluences.

### 3. Conclusion

In conclusion, we have found that alloying Sb into Cs$_2$AgSbX$_6$ leads to a reduction in photovoltaic performance due to the introduction of sub-bandgap states ≈0.7 eV below the optical bandgap. Thus, although Sb alloying leads to a reduction in the bandgap of Cs$_2$AgBiBr$_6$, the $V_{OC}$ is reduced by 0.7 V due to charge carriers depopulating the band states to the sub-bandgap state, leading to a reduction in the quasi-Fermi level splitting. The shorter charge-carrier lifetimes also led to reduced EQEs, and hence lower $J_{SC}$. Furthermore, the absorption strength at the indirect bandgap is low in these elpasolites, and the reductions in bandgap do not give a sizeable increase in EQE at longer wavelengths. Through detailed Williamson–Hall analysis, we found that introducing Sb into Cs$_2$AgBiBr$_6$ leads to an increase in strain in these films, which is likely due to the smaller size of the Sb$^{3+}$ cation compared to the Bi$^{3+}$, and is likely a cause of the sub-bandgap state introduced. We found that we could relieve the strain introduced through aerosol annealing, and that this could reduce (but not eliminate) the density of sub-bandgap states, and slow down the depopulation of charge carriers from the excited state. This work shows the limitations of Sb alloying as a strategy to reduce the bandgap of Cs$_2$AgBiBr$_6$, and emphasizes the importance of controlling strain in compositional engineering efforts to tune the properties of halide elpasolite films.

### 4. Experimental Section

#### Synthesis of Cs$_2$AgSb$_x$Bi$_{1-x}$Br$_6$ Thin Films

The procedure for synthesizing these films is based on our previously reported method reported in ref. [14]. Separate solutions containing Bi only, and Sb only were prepared in DMSO. For the precursor solution containing only Bi in the precipitogen site, 1.5 mmol CsBr (99.9%, Sigma Aldrich), 0.73 mmol AgBr (99.998%, Alfa Aesar), 0.75 mmol BiBr$_3$ (99.98%, Sigma Aldrich) were dissolved in 1.5 mL anhydrous DMSO (99.5%, Sigma Aldrich) and mixed at 700 rpm at room temperature inside an N$_2$-filled glovebox for 1 h. For the precursor solution with only Sb in the precipitogen site, 0.75 mmol SbBr$_3$ (99.99%, Sigma Aldrich) was mixed with 1.5 mmol CsBr and 0.75 mmol AgBr. This solution was also mixed at 700 rpm at room temperature inside an N$_2$-filled glovebox for an hour. Both solutions were subsequently filtered through a 0.2 µm PTFE membrane filter (Sigma Aldrich), and either directly used for growing Cs$_2$AgBiBr$_6$ and Cs$_2$AgSb$_{1-x}$Bi$_x$Br$_6$ or mixed (450 µL Sb-based solution + 50 µL Bi-based solution) to achieve Cs$_2$AgSb$_{0.9}$Bi$_{0.1}$Br$_6$. It was previously shown that the nominal stoichiometry in solution matched the bulk composition of the films.[14]

The substrates used for characterization were borosilicate glass (for PL measurements) or quartz (for XRD and PDS measurements). These substrates were cleaned by ultrasonication in acetone, followed by propan-2-ol, for 15 min each. Afterward, the substrates were dried by flowing compressed dry air before O$_2$ plasma treatment for 10 min (300 W forward power, 0 W reverse power). These substrates were subsequently taken inside an N$_2$-filled glovebox and heated at 75 °C. The Sb-containing solutions were kept at room temperature, whereas the Bi-only solution was preheated to 75 °C on a hotplate. To deposit the films, the substrate was placed onto a vacuum-free check, and 60 µL solution was dropped immediately, before spinning at 4000 rpm for 15 s. Cs$_2$AgSbBr$_6$ and Cs$_2$AgSb$_{0.9}$Bi$_{0.1}$Br$_6$ were subsequently annealed at 135 °C for 5 min inside an N$_2$-filled glovebox, whereas Cs$_2$AgSb$_{1-x}$Bi$_x$Br$_6$ was annealed at 250 °C for 5 min. For the antisolvent-treated films, 150 µL of toluene was dropped quickly onto the spinning substrate 15 s after the start of spinning.

Photovoltaic Device Fabrication and Characterization: Fluorine-doped tin oxide (FTO) coated glass (Sigma Aldrich) was patterned by etching with 2 mol L$^{-1}$ HCl (Fisher Chemical) and Zn powder (98%, Sigma Aldrich). The substrates were subsequently cut to 14 mm × 14 mm squares and cleaned with 2% Hellmanex solution, being rinsed with deionized water and ethanol. They were cleaned in the same way as the glass/quartz substrates described earlier, but with 5 min of O$_2$ plasma treatment.

A blocking layer of TiO$_2$ was subsequently deposited by spray pyrolysis. The substrates were placed on a hotplate and heated to 450 °C. For spray pyrolysis, the precursor solution was made by mixing 0.4 mL acetylacetone (99%, Alfa Aesar), 0.6 mL titanium disopropoxide bis(acetylacetone) (75 wt% in isopropanol, Sigma Aldrich) and 9 mL ethanol. The substrates were distributed over the hotplate, and the solution was evenly sprayed over the entire hotplate, with the tube held 20 cm away from the hotplate, at an angle of 45°. The spraying was repeated every 20 s, over a period of 20 min. The substrates were subsequently cooled naturally to 150 °C, before they were removed from the hotplate. To deposit the mesoporous TiO$_2$ layer, TiO$_2$ paste (Dyesol) was dissolved in ethanol at 150 mg mL$^{-1}$. 30 µL of this solution was subsequently dropped onto the TiO$_2$-coated FTO, then spun at 4000 rpm for 10 s. The substrates were annealed on a hotplate with a gradual ramp up in temperature (5 min ramp up to 125 °C, hold for 5 min, 15 min ramp up to 325 °C, hold for 5 min, 5 min ramp up to 375 °C, hold for 5 min, 5 min ramp up to 450 °C, hold for 30 min), before being naturally cooled to 150 °C and removed from the hotplate. The TiO$_2$-coated substrates were immediately taken into an N$_2$-filled glovebox, where the halide elpasolite films were deposited following the procedure detailed earlier.

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**Table 2.** Fitting parameters from a phenomenological biexponential fit to the GSB kinetics from TA measurements of pristine and aerosol-annealed Cs$_2$AgSb$_{0.9}$Bi$_{0.1}$Br$_6$ thin films. The model was $I_t = A_1 \exp\left(-\frac{t}{\tau_{G1}}\right) + A_2 \exp\left(-\frac{t}{\tau_{G2}}\right)$, where $I_{G1}$ is the normalized GSB signal, $A_1$ and $A_2$ the pre-exponential constants, $\tau_1$ and $\tau_2$ the time constants of this model, and $\tau_0$ the time at which the GSB reaches its peak signal after photo-excitation. The effective time-constant $\tau_{eff}$ was the average between $\tau_1$ and $\tau_2$, weighted by the pre-exponential constant.

| Aerosol annealing temperature [°C] | Excitation fluence [µJ cm$^{-2}$ pulse$^{-1}$] | A$_1$ [-] | r$_1$ [ns] | A$_2$ [-] | r$_2$ [ns] | $\tau_{eff}$ [ns] |
|-----------------------------------|-----------------------------|-----|------|-----|------|--------|
| None (pristine)                   | 53                          | 0.45 | 3.4  | 0.73 | 147  | 92     |
| 100                               | 93                          | 0.62 | 58.0 | 0.31 | 388  | 239    |
| 125                               | 53                          | 0.61 | 60.4 | 0.29 | 477  | 196    |
| 150                               | 93                          | 0.60 | 58.0 | 0.31 | 388  | 170    |
The hole transport layer (HTL) was used poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine], or PTAA (EM Index). The additives used were a solution of 51.7 mg mL$^{-1}$ bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI, 99% from Sigma Aldrich) in acetonitrile, and a solution of 100 μL mL$^{-1}$ 4-tert-butylpyridine (tBP, 96%, Sigma Aldrich) in toluene. The HTL solution was prepared in an N$_2$-filled glovebox by mixing together 10 mg PTAA, 16 μL Li-TFSI solution, and 20 μL tBP solution with 964 μL toluene. This solution was shaken until fully dissolved. The HTL was deposited by dropping 40 μL PTAA solution onto the halide elpasolite film and spun at 1500 rpm for 20 s. To complete the devices, 100 nm of gold was thermally evaporated on top of the devices.

The device area was defined by the 4.1 mm$^2$ aperture area in which the metal top electrode and bottom FTO electrode overlapped. Solar simulations were performed using a calibrated ABET Technologies Sun 2000 solar simulator, with I–V sweeps made using a Keithley 2623 A source-measure unit. EQE measurements were made using a 300 W Xenon lamp (ILC Technology) for the light source, which was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd.), and the same Keithley source-measure unit was used to measure the photocurrent produced in the device.

Characterization of Cs$_2$AgSb$_{1−x}$Bi$_x$: Thin Films: XRD measurements were performed using a PANalytical X’Pert Pro diffractometer using Ni-filtered Cu K$_\alpha$ X-rays (λ = 1.5406 Å). Diffractograms were obtained from 5°–70° 2θ with a step size of 0.016°. SEM measurements were made using a LEO 1530 VP instrument. The acceleration voltage was 3 kV, with 10$^{-3}$ Pa as the chamber vacuum. All samples had Au/Pd deposited on top to prevent charge accumulation, and this was deposited using an Emitech sputter coater (65 mA current for 7 s). PDS measurements were made according to previous reports, and these are detailed in ref. [39]. Samples were prepared on quartz substrates, and these immersed in a FC-72 Fluorinert (3M Company) medium. The sample was pumped with chopped monochromated light of different wavelengths, and a fixed wavelength continuous wave (cw) laser probe was passed through the refractive index gradient in the liquid medium, with a deflection proportional to the absorbance of the pump light at a particular wavelength by the sample. PL measurements were performed using an intensified charge-coupled device camera (iCCD) using an Andor iStar DH740 CCI-010 system connected to a grating spectrometer (Andor SR303i). The films, deposited on glass, were excited with a 400 nm wavelength pump laser, produced using a frequency-doubled Ti:sapphire laser (Spectra-Physics Solstice). The repetition rate was 1 kHz and the pulse length was ≈100 fs. The slit width in the spectrometer was 400 μm, exposure time 0.3 s, and the number of accumulations 15. TA spectroscopy measurements were performed using 355 nm wavelength pump pulses with a pulse width of ≈800 ps. These were provided by an electronically controlled, Q-switched Nd:YVO$_4$ laser (Innolas Picolo 25). Broadband probe pulses (380–620 nm wavelength) were generated by focusing an 800 nm wavelength fundamental laser onto a CaF$_2$ crystal controlled by a digital motion controller (Mercury C-863 DC Motor Controller). The repetition rate of the pump pulses was 1 kHz, but the transmittance with and without pump excitation (T$^{\text{pump on}}$ and T$^{\text{pump off}}$) through the samples was collected at a rate of 500 Hz, which was controlled by a chopper wheel rotating. The transmitted pulses were collected by a monochrome line scan camera (JAI SW-4000M-PMCL; spectrograph, Andor Shamrock SR-163). These transmittances were used to calculate the TA signal intensity, ΔT = T$^{\text{pump on}}$ - T$^{\text{pump off}}$.

Aerosol-Assisted Post-Annealing: The films were post-treated in a custom-made stainless steel reactor at temperatures ranging from 100–150°C in a well-ventilated fume hood. A 50:50 volume ratio of DMF and DMSO solvent was used for the process. After the films were placed in the preheated reactor, N$_2$ gas at a flow rate of 0.5 dm$^3$ min$^{-1}$ was used to carry aerosols of the DMF:DMSO solvent into the reactor. The aerosol-assisted solvent treatment process was conducted for 5 min, after which the reactor was cooled down to room temperature. Post-treatment annealing was conducted in an N$_2$-filled glovebox and the films were annealed at 150°C for 5 min.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are openly available in Imperial Research Data Repository at http://dx.doi.org/10.14469/hpc/11108, reference number 11108.

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