Supporting Information

Composition Stoichiometry of Cs$_2$AgBiBr$_6$ Films for Highly Efficient Lead-Free Perovskite Solar Cells

Femi Igbari†#, Rui Wang†#, Zhao-Kui Wang†*, Xing-Juan Ma†, Qiang Wang†, Kai-Li Wang†, Yue Zhang†, Liang-Sheng Liao†*, and Yang Yang†*

† Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou, Jiangsu 215123, China

‡ Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, USA.

#F.I. and R.W. contributed equally to this work.

*Address correspondence to Z.K.W (email: zkwang@suda.edu.cn) or to L.S.L (email: lsliao@suda.edu.cn) or to Y.Y. (email: yangy@ucla.edu).

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Experimental Section

Materials: 15 Ω/sq Fluorine doped tin oxide (FTO) glass substrates, TiCl₄, 2,2,7,7-Tetrakis (N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (SpiroOMeTAD), and Lithium bis(trifluoromethanesulfonyl)imideanhydrous (Li-TFSI) were purchased from You Xuan Company. CsBr (99.9%), 4-tertbutylpyridine (tBP), Dimethyl sulphoxide (DMSO) and Chlorobenzene were bought from Sigma Aldrich. AgBr (99.99%), BiBr₃ (99%), hydrobromic acid, and HBr (40% in water) were purchased from Alfa Aeser. As presented, all the purchased precursor materials and solvents were used as received with no further purification.

Solution-processed Cs₂AgBiBr₆ film: Crystalline powder of Cs₂AgBiBr₆ was prepared by keeping the ratio 2:1:1 of CsBr:AgBr:BiBr₃ via dissolving 213 mg of CsBr, 94 mg of AgBr and 225 mg of BiBr₃ in 20 mL of HBr (48% in water) while stirring and allowing the mixture to react at the boiling point of HBr (122 °C) under reflux for 1 hr. About half of the HBr solvent was then evaporated off at the same temperature for an additional 2 hrs while stirring. The obtained solution was allowed to cool to room temperature overnight in a dry and dark atmosphere. The orange crystalline powder of Cs₂AgBiBr₆ obtained (Figure S1a) was simply separated from the mother liquor by decanting. The crystalline powder was then washed three times with absolute ethanol and was dried for 24 hrs. 0.5 M solution of the Cs₂AgBiBr₆ powder was prepared at room temperature, using DMSO as solvent. A light-yellow solution was obtained (Figure S1b). The Cs₂AgBiBr₆ absorber layer was deposited via spin-coating. Drops of the prepared solution were spun on the TiO₂ layer at 4000 rpm for 40 sec. The obtained films were annealed at 240 °C, 260 °C, 280 °C and 300 °C for 5 min, to determine the optimum annealing temperature.

Vacuum-sublimated Cs₂AgBiBr₆ film: Multiple cycles of sequential deposition of CsBr, AgBr and BiBr₃ precursor materials were carried out under vacuum conditions at a base pressure of 5.0
$3 \times 10^{-4}$ Pa. The precursors (Figure S1d, e and f) were placed in three separate sources in the vacuum chamber. To achieve film uniformity and maintain the 2:1:1 ratio of the precursor compounds in the resulting halide double perovskite film, the following precautions were taken: the sensor was positioned at an equal distance. The thickness of the ultrathin layer of each precursor and the deposition rate was derived by preliminarily obtained parameters (i.e. mole ratio, molar masses and densities of precursors and substrate surface area). Details are given in Table S1. Corresponding adjustments were made to the thickness of films actually deposited to make for the difference (details are given in Table S2). Five deposition cycles of the CsBr, AgBr and BiBr$_3$ layers, each with mole ratio of 2:1:1 were made to finally achieve a multiple CsBr/AgBr/BiBr$_3$ stack with an overall film thickness about 200 nm. The film was subsequently annealed at 180 °C, 200 °C, 220 °C and 240 °C for 30 min to obtain the optimum annealing temperature for Cs$_2$AgBiBr$_6$ double perovskite crystal phase.

**Device fabrication:** FTO glass was successively cleaned in soapy water, deionized water, acetone and ethanol in an ultrasonic bath. Each cleaning cycle took 15 min. A compact TiO$_2$ electron transport layer (ETL) was deposited on the treated FTO substrate by a chemical bath deposition method. 0.074 M solution of SpiroOMeTAD (in Chlorobenzene) doped with 1.81 M Li-TFSI (in acetonitrile) and tBP was then deposited on the absorber layers obtained by the two aforementioned deposition pathways via spin-coating at 5000 rpm for 60 sec. Finally, 10 nm MoO$_3$ film and 100 nm Ag electrode were deposited by vacuum evaporation at a rate of 0.04 nm/s and 0.1 nm/s respectively. A shadow mask which patterned the electrode and gave the devices an active area of 0.09 cm$^2$ was used.

**Measurement and Characterization:** The crystallinity of the Cs$_2$AgBiBr$_6$ films obtained by the two processes was measured using Empyrean X-ray diffractometer (XRD) with monochromatic
Cu Kα irradiation with a wavelength, 1.5406 Å. Scanning electron microscope (SEM) images of the Cs$_2$AgBiBr$_6$ layers were obtained on ZEISS SUPRA 55 field-emission electron microscope under high vacuum with an electron energy of 10 keV. Film thicknesses and surface morphology were measured by atomic force microscopy (AFM) using Oxford Instrument Asylum Research in the tapping mode. UV-Vis absorption spectra were obtained by using PerkinElmer UV-Vis spectrophotometer. The stoichiometry of the chemical composition of the Cs$_2$AgBiBr$_6$ films was determined by XPS using Kratos Analytical Himadzu X-ray photoelectron spectrometer. Steady-state PL and time-resolved PL measurement were conducted on a Horiba Scientific FluoroHub single photon counting controller. Current density-voltage ($J$-$V$) curves and external quantum efficiency (EQE) measurements were obtained on a Keithley semiconductor parameter analyzer under simulated AM 1.5G irradiation (100mWcm$^{-2}$, xenon lamp, Newport).
Figure S1. Precursor materials and thin films of solution- and vacuum-processed Cs$_2$AgBiBr$_6$. (a), (d), (e) and (f) are Cs$_2$AgBiBr$_6$, CsBr, AgBr and BiBr$_3$ powders respectively. (b) is Cs$_2$AgBiBr$_6$ solution in DMSO. (c) and (g) are thin films obtained by spin coating and vacuum deposition respectively.
Thickness of Ultrathin Films

The required thickness of ultrathin layer of each precursor material was determined by Equations S1, S2 and S3.

\[
\rho = \frac{m}{v} \quad \ldots \quad \text{(S1)}
\]

\[
m = n \times M \quad \ldots \quad \text{(S2)}
\]

\[
v = l \times b \times h \quad \ldots \quad \text{(S3)}
\]

Where $\rho$ is the density, $m$ is the mass, $n$ is the mole ratio and $M$ is the molar mass of precursor material, $v$ is the volume and $h$ is the height (thickness) of ultrathin film, $l$ is the length, $b$ is the breadth of the substrate.

Table S1. Ultrathin film thickness determination parameters.

| Precursor materials | CsBr | AgBr | BiBr$_3$ |
|---------------------|------|------|----------|
| $\rho$ (g/cm$^3$)   | 4.43 | 6.47 | 5.70     |
| $n$                 | 2    | 1    | 1        |
| $M$ (g/mol)         | 212.81 | 187.77 | 448.69 |
| $l$ (mm)            | 25   | 25   | 25       |
| $b$ (mm)            | 20   | 20   | 20       |

Table S2. Ultrathin film thickness correction parameters.

| Precursor materials | CsBr | AgBr | BiBr$_3$ |
|---------------------|------|------|----------|
| Predicted $h$ (nm)  | 19.2 | 5.8  | 15.7     |
| Deposited $h$ (nm) (1st) | 19.2 | 5.8  | 15.7     |
| Measured $h$ (nm) (AFM) | 17.3 | 5.1 | 13.2 |
|--------------------------|------|-----|------|
| Error (%)                | 10   | 13  | 16   |
| Correction               | +1.9 | +0.7| +2.5 |
| Deposited $h$ (nm) (2nd) | 21.1 | 6.5 | 18.2 |
| Actual $h$ (nm)          | 19.2 | 5.8 | 15.7 |

**Calculation of Grain Size of Crystallites**

Value of the full width at half maximum (FWHM) of the most intense peak in each XRD pattern was substituted into the Scherrer equation.

$$\beta (2\theta) = \frac{k\lambda}{L \cos \theta} \quad \text{(S4)}$$

$\beta = \text{line broadening FWHM (rad)}$

$2\theta = \text{peak position (rad)}$

$k = \text{shape factor (dimensionless)}$

$\lambda = \text{X-ray wavelength (nm)}$

$L = \text{mean size of crystalline domains (nm)}$

**Table S3.** Determination of annealing temperature dependent crystalline domain sizes of the solution and vacuum processed Cs$_2$AgBiBr$_6$ thin films.

| Thin film                  | Annealing temperature (°C) | FWHM (θ) | FWHM (rad) | Domain (nm) |
|---------------------------|-----------------------------|-----------|-------------|-------------|
| Solution-processed        | 240                         | 0.57      | 0.0100      | 139         |
|                           | 260                         | 0.40      | 0.0070      | 198         |
|                           | 280                         | 0.34      | 0.0060      | 232         |
|                           | 300                         | 0.40      | 0.0070      | 198         |
| Vacuum-processed          | 180                         | 0.68      | 0.0113      | 123         |
|                           | 200                         | 0.49      | 0.0085      | 164         |
Peak position (2θ): 31.75 (°), θ: 15.88 (°) = 0.28 (rad)

Shape factor (k): 0.9

X-ray wavelength (λ): 1.5406 Å = 0.15406 (nm)

**Figure S2.** Plan view SEM images of the solution-processed films annealed at (a) 240 °C, (b) 260 °C, (c) 280 °C and (d) 300 °C and vacuum-processed films annealed at (e) 180 °C, (f) 200 °C, (g) 220 °C and (h) 240 °C.
**Figure S3.** AFM images of the optimized (a) vacuum- and (b) solution-processed Cs$_2$AgBiBr$_6$ thin films annealed at 220 °C and 280 °C respectively.
Figure S4. Detailed XPS scans of Ag 3d and Bi 4f core levels of (a) solution- and (b) vacuum-processed Cs$_2$AgBiBr$_6$ thin film.
**Figure S5.** Deviation of the atomic ratios of the chemical composition of solution- and vacuum-processed $\text{Cs}_2\text{AgBiBr}_6$ thin films from ideality.
Figure S6. XRD patterns of freshly prepared and high temperature aged (300 hrs) Cs$_2$AgBiBr$_6$ thin films for (a) solution-processing and (b) vacuum-sublimation.
Determination of Mobility

Fick’s Law in **Equation S5** was taken as an equation for a straight line graph $y = mx + c$. Where $y$ stands for $J$, $m$ (slope) is $D$, $x$ is $\frac{dc}{dx}$ and $c$ is taken as zero ($0$). Slopes of the long-lived portions of the decay curves were obtained and their absolute values were taken as the diffusivities of the films.

$$J = -D \frac{dc}{dx} \text{...........................................}(S5)$$

The values were substituted in to Einstein’s relation in **Equation S6** to obtain the mobilities of photoexcited charges in the films.

$$D = \frac{\mu k T}{q} \text{...........................................}(S6)$$

Where $\mu$ is the mobility, $k$ is Boltzmann’s constant, $T$ is absolute temperature and $q$ is electrical charge.
Figure S7. $J$-$V$ curve of solution- and vacuum-processed devices based on the optimization of annealing temperature.
Table S4. PV parameters of solution- and vacuum-processed perovskite solar cells based on the optimization of annealing temperature.

| Device   | Temperature (°C) | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF  | PCE (%) |
|----------|------------------|-----------------------|--------------|-----|---------|
| Solution | 240              | 3.19                  | 1.01         | 0.54| 1.74    |
|          | 260              | 3.61                  | 1.01         | 0.63| 2.30    |
|          | 280              | 3.82                  | 1.01         | 0.65| 2.51    |
|          | 300              | 3.40                  | 1.01         | 0.64| 2.19    |
| Vacuum   | 180              | 1.39                  | 1.05         | 0.56| 0.82    |
|          | 200              | 1.81                  | 1.05         | 0.63| 1.20    |
|          | 220              | 2.06                  | 1.05         | 0.65| 1.41    |
|          | 240              | 1.60                  | 1.05         | 0.62| 1.04    |
Figure S8. The distribution of PCEs of the (a) solution- and (b) vacuum-processed devices.
Figure S9. J-V curves showing the hysteretic responses of the (a) solution and (b) vacuum processed champion cells.