Highly Absorbing Lead-Free Semiconductor Cu$_2$AgBiI$_6$ for Photovoltaic Applications from the Quaternary CuI-AgI-BiI$_3$ Phase Space

Harry C. Sansom, Giulia Longo, Adam D. Wright, Leonardo R.V. Buizza, Suhas Mahesh, Bernard Wenger, Marco Zanella, Mojtaba Abdi-Jalebi, Michael J. Pitcher, Matthew S. Dyer, Troy D. Manning, Richard H. Friend, Laura M. Herz, Henry J. Snaith, John B. Claridge, Matthew J. Rosseinsky

1. University of Liverpool, Department of Chemistry, Crown St., Liverpool L69 7ZD, U.K.
2. University of Oxford, Clarendon Laboratory, Department of Physics, Parks Road, Oxford OX1 3PU, U.K.
3. University College London, Institute for Materials Discovery, Malet Place, London WC1E 7JE, U.K.
4. University of Cambridge, Cavendish Laboratory, JJ Thomson Avenue, Cambridge CB3 0HE, U.K.

Present Addresses

† Northumbria University, Department of Mathematics, Physics and Electrical Engineering, Ellison Place, Newcastle upon Tyne NE18ST, U.K.
‡ CEMHTI CNRS UPR3079, 45071 Orléans, France
Cu$_2$AgBiI$_6$ powder and crystal synthesis

The starting materials used were CuI (99.999% Sigma–Aldrich) and AgI (99.999% Alfa Aesar). BiI$_3$ and AgBiI$_4$ were synthesised as previously reported.$^1$ Powder synthesis was carried out in evacuated sealed fused silica tubes. The fused silica tubes had a 6 mm internal diameter, 1 mm thick walls and were sealed at 10$^{-4}$ mbar to 15 cm in length. The sample in the tube was cooled in liquid N$_2$ during the evacuation and sealing process to avoid sublimation of the iodides. CuI (0.0728g), AgI (0.0505g) and BiI$_3$ (0.1268g) powders (nominal composition Cu$_{1.18}$Ag$_{0.6}$Bi$_{1.24}$I$_{6.06}$) were dissolved in the evacuated fused silica tube. The tube was placed upright in a furnace and heated at 5°C/min to 610°C and kept there overnight before cooling at 5°C/min to 350°C where it was kept for 5 days. It was then cooled to room temperature at 5°C/min. The tube was scored and carefully broken open to retrieve the black powder, which was pelletised in to pellets 5 mm in diameter using a pellet press. The pellets were sealed in an evacuated fused silica tube. The second heating consisted of heating the powder up at 5°C/min to 350°C, keeping it there for 5 days before taking the tube out of the furnace and quenching the bottom half of it (containing the powder) to room temperature in a water bath. It was found to be crucial to quench the material from 350°C and keep the annealing temperatures below the melting point of the mixture to avoid a compositional inhomogeneity which spanned the Cu$_2$AgBiI$_3$$_x$I$_{4-x}$ solid solution line (Figures S1a and b). The tube was scored and carefully broken open to retrieve the black powder. A small crystal of approximate dimensions 20 μm × 30 μm × 10 μm, with an average SEM EDX composition 0.2418 g of AgI (1.03 mmol), 0.2381 g of CuI (1.25 mmol) and 0.5172 g of BiI$_3$ (0.877 mmol), corresponding to composition Cu$_{1.15}$Ag$_{1.28}$Bi$_{1.27}$I$_{6.06}$. The films were then annealed at 150°C for 3 minutes. The films had a thickness of 280 nm, measured using a profilometer.

Cu$_2$AgBiI$_6$ device fabrication

Fluorine doped tin oxide (FTO) coated glass (15 Ω/sq) were etched using a 2M HCl solution and Zn powder. The patterned FTO substrates were cleaned through sequential sonication in soap, deionized water, acetone and isopropanol. The substrates were dried with a N$_2$ gun and exposed to O$_2$ plasma for 10 minutes. The SnO$_2$ electron transport layer was prepared by spin-coating a solution of SnCl$_2$·5H$_2$O in isopropanol (17.5 mg/ml) on top of the FTO coated glasses using 3000 rpm speed for 30 seconds. The so-prepared films were annealed at 100°C for 10 min followed by an annealing at 180°C for 30 min in air. After this the Cu$_2$AgBiI$_6$ film was deposited as explained in the thin film deposition. The hole transport material (SpiroOMeTAD, Lumtec) was dissolved in chlorobenzene (85 mg/ml) and doped with 20 μl of LiTFSI (500 mg/ml in butanol) and with 30 μl of tert-butylpyridine. This solution was then deposited on the Cu$_2$AgBiI$_6$ layer by dynamic spin-coating in air at 2000 rpm for 45 seconds. The devices were then left overnight in a dry air atmosphere, and then completed by the evaporation of 100 nm silver contacts. The device architecture is shown inset in Figure 4b. Device characterisations were performed in air unless specified otherwise.

Powder X-ray diffraction (PXRD)

PXRD data were measured on a Panalytical X`Pert Pro diffractometer using Co Kα$_1$ radiation ($\lambda = 1.7890$ Å) in Bragg–Brentano geometry and an X'Celerator detector. Phase identification was carried out using the X'Pert HighScore Plus (Version 2.2a)$^2$ with the PDF-2-ICDD database. PXRD data of capillaries used for photostability assessment were measured on a Bruker D8 Advance diffractometer using monochromated Mo Kα$_1$ radiation ($\lambda = 0.7093$ Å). TopasAcademic (Version 5) was used to perform Pawley fittings and Rietveld refinements of the data. VESTA$^3$ was used for graphical representation of the structures.
Single crystal X-ray diffraction (SCXRD)

Data were collected at 100K on a Rigaku MicroMax-007 HF diffractometer with a molybdenum rotating anode microfocus source and a Saturn 724+ detector using Rigaku Crystal Clear v2.0. Unit-cell indexation, data integration, and reduction were performed using Rigaku CrysAlisPro v171.38.43. The structure was solved and refined using SHELX-2013, implemented through Olex2.

Compositional Analysis

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) was used to measure the composition as a direct elemental analysis technique. Measurements were carried out using a Hitachi S-4800 SEM with an Oxford Instruments model 7200 EDS X-ray detector. Quantification was carried out using the microanalysis suite of the Inca Suite software (Version 4.15). All powders and crystals were sputtered with 15 nm Au to limit charging effects. Transmission Electron Microscopy (TEM) EDX was carried out using an JEOL JEM 2000FXII TEM microscope operating a W electron source operated at 200 kV, using an EDAX EDX detector, with quantification carried out using EDAX Genesis Spectrum (Version 5.217, 21-Jan-2008). All samples were prepared by spreading a finely ground powder onto carbon coated Au grids. Beam intensity had to be lowered, by increasing the spot size of the beam, to not decompose the samples. All compositions calculated from EDX measurements were normalised to the nominal iodide content unless otherwise stated. The one standard deviation (1σ) spread in compositions measured for powder standards CuI and AgI, as well as was the synthesised BiI₃, CuBiI₃ and Cu₂AgBiI₆ samples, are shown in Table S4.

Photostability

For the experiments, a Solar Light Model 165-300-002 Solar Simulator was used which has a spectral output that complies with air mass 1.5 (AM1.5) per the ASTM standard definition. The combination of neutral density filters and lamp-to-sample distance allowed for the tuning of the intensity of the incident light to 1000 W m⁻² as measured by a Solar Light Pyranometer PMA2144 and datalogging radiometer PMA2100. Sample temperatures were monitored using a T-type thermocouple and were found to stay below 35°C. For measurements in sealed atmospheres, powder was loaded into thin-walled (0.01 mm wall thickness) borosilicate capillaries under ambient air, dry synthetic air, and helium, and these were sealed with a gas-oxygen torch. The capillaries were then placed in the solar simulator and subjected to the full solar spectrum at an intensity of 1000 W m⁻².

Raman Spectroscopy

The measurements were carried out on a Renishaw inVia Reflex with a Leica microscope utilising a 633 nm wavelength red laser with a maximum power of 6.5 mW. The powder samples were measured in borosilicate capillaries and were exposed to 0.5% of the maximum laser power to avoid decomposition of the sample. The spot size was 5 µm.

Photoluminescence (PL) Spectroscopy

The Cu₂AgBiI₆ film was mounted in a gas-exchange helium cryostat (Oxford Instruments, OptistatCF2) and photoexcited by a 398 nm picosecond pulsed diode laser (Picoquant, LDH-D-C-405M). The resultant PL was collected and coupled into a grating spectrometer (Princeton Instruments, SP-2558), which directed the spectrally dispersed PL onto a photon-counting detector (PDM series from MPD), whose timing was controlled with a PicoHarp300 TCSPC event timer. A laser fluence of 200 nJ cm⁻² was used for both the spectral and transient measurements of Cu₂AgBiI₆, which were both taken at a temperature of 295 K. The PL decay trace in Figure S16b was measured at a wavelength of 720 nm. The PL decay trace was fitted by a stretched exponential function $I = I_0 \exp(-t/\tau)^\beta$, where $\beta$ is the distribution coefficient and $\tau$ is the time taken for the PL intensity to drop to $I_0/e$. Such stretched exponential functions have been used to phenomenologically account for the presence of a local distribution of monoexponential decay rates, whose average lifetime is given by $\tau_{av} = (\tau/\beta) f(1/\beta)$, where $f$ is the gamma function.

The PL spectrum for MAPbI₃ in Figure S15 was measured using the same experimental setup, except it was mounted in a cold-finger cryostat (Oxford Instruments, MicrostatHe) and detected with an ICCD (PI-MAX4, Princeton Instruments), under a laser excitation fluence of 490 nJ cm⁻². The spectrum was previously published in Wright et al.

UV-Visible absorption measurements using FTIR spectrometer

The UV-Visible absorption spectra in Figure 3 in the main text were measured using a Bruker Vertex 80v Fourier transform infrared (FTIR) spectrometer, configured with a tungsten halogen lamp illumination source, a CaF₂ beam splitter and a silicon detector. The samples were mounted in a gas-exchange helium cryostat (Oxford Instruments, OptistatCF2). The MAPbI₃ absorption spectrum was previously published in Davies et al.

THz photoconductivity

An amplified laser system (Spectra Physics, MaiTai–Empower–Spitfire) with a central wavelength of 800 nm, 35 fs pulse duration and 5 kHz repetition rate was used to generate THz radiation via the inverse spin Hall effect, using an emitter made of 2 nm of tungsten / 1.8 nm of Cu₂Fe₃O₆B₂O₇ / 2 nm of platinum, supported by a quartz substrate. The transmitted THz radiation was detected using free-space electro-optic sampling with a 1 mm thick ZnTe (110) crystal, a Wollaston prism and a pair of balanced photodiodes. The THz pulse was measured in transmission geometry. The pump beam was frequency-doubled to 400 nm by a β-barium-borate (BBO) crystal. Charge-carrier mobilities
were calculated from the initial transmitted signal at time = 0 ps at fluences of 7.8, 15.3 μJ/cm², as outlined in Wehrenfennig et al.,¹⁰ and measurements were carried out under vacuum (< 10⁻² mbar).

**J–V characterisation**

J–V characterisation was measured using a Keithley 2400 sourcemeter and simulated air-mass 1.5 global tilt (AM1.5G) solar irradiation using a Wavelabs Sinus-220 light-emitting diode array, calibrated with a certified Si reference cell. The areas being measured were defined by using a black anodised aluminium mask placed directly in contact with glass side of the substrate and an enclosed sample holder, to shadow the rest of the device.

**Photothermal deflection spectroscopy (PDS)**

PDS is an ultrasensitive absorption measurement technique that detects heating of the sample due to the non-radiative relaxation of absorbed light and is insensitive to reflection and scattering. PDS enables the detection of absorbance signals with 5–6 orders of magnitude weaker than the band edge absorption. For the measurements, a monochromatic pump light beam is shined on the sample (film on Quartz substrate), which on absorption produces a thermal gradient near the sample surface via non-radiative relaxation induced heating. This results in a refractive index gradient in the area surrounding the sample surface. This refractive index gradient is further enhanced by immersing the sample in an inert liquid FC-72 Fluorinert® (3M Company) which has a high refractive index change per unit change in temperature. A fixed wavelength CW laser probe beam is passed through this refractive index gradient producing a deflection proportional to the absorbed light at that particular wavelength, which is detected by a photo-diode and lock-in amplifier combination. Scanning through different wavelengths gives us the complete absorption spectra. Because this technique makes use of the non-radiative relaxation processes in the sample, it is immune to optical effects like interference and scattering. Furthermore, PDS technique is a powerful technique to measure the sub-bandgap tail states in a semiconductor up to an absorption coefficient of 1 cm⁻¹.

**Elliott Model Fitting**

We use Elliott’s formula¹¹ which expresses the absorption coefficient as a linear combination of the absorption of a bound exciton with the absorption by the joint continuum of states⁹,¹²:

\[
a(E) = a_x(E) + a_{\text{cont}}(E)
\]

with

\[
a(E) = \frac{2(2\mu)^2e^2}{ncm_0^2\hbar^3} |P_{\text{cel}}|^2 \int_0^\infty \frac{4\pi E_3^{3/2}}{n^3} \delta \left( E - \left( E_g - \frac{E_x}{n^2} \right) \right) \left[ 1 - \exp \left( -\frac{2\pi E_x}{E - E_g} \right) \right] \Theta \left( \frac{E - E_g}{\sqrt{E - E_g}} \right) \sum_{n=1}^\infty \frac{\delta \left( E - \left( E_g - \frac{E_x}{n^2} \right) \right)}{n^3}
\]

Where \( E \) is the photon energy, \( E_x \) is the exciton binding energy, \( E_g \) is the band gap, \( n \) is the refractive index (at energy \( E \)), \(|P_{\text{cel}}|^2 = |\langle \Psi_{\text{el}} | P | \Psi_{\text{p}} \rangle|^2\) is the momentum matrix element, \( \delta \) is the Dirac delta function, \( \Theta(x) \) is the step function, \( \mu \) is the reduced mass, \( m_0 \) is the electron rest mass, \( e \) is the elementary charge, \( c \) is the speed of light in vacuum and \( \hbar \) is the reduced Planck’s constant.

The experimental absorption spectrum is fitted with the following model:

\[
a(E) = \frac{A}{E} \left[ (a_x * g_x)(E) + (a_{\text{cont}} * g_{\text{cont}})(E) \right]
\]

Where \( A \) is a fitting constant and the excitonic part of the absorption \((a_x')\) and the continuum part \((a_{\text{cont}}')\) are convoluted with gaussian broadening functions \( g_x \) and \( g_{\text{cont}} \), respectively.

**Optical Modelling**

The generalised transfer matrix method was used to model the optical response of the stack.¹³ The python libraries Numpy and Scipy were used to perform the calculations. Transfer matrix calculations take the complex refractive index spectrum and thickness for each layer as input. The calculation provides us with absorptance of each layer, and the transmittance and reflectance of the stack. We assumed perfect internal quantum efficiency and calculated the short circuit current \( J_{sc} \) as the overlap integral of the AM1.5 solar spectrum with the absorptance. The JV curve of each sub-cell was modelled as a single diode: \( J = J_{sc} - J_0 e^{\frac{qV}{nkT}} \). Here, \( n \) is the ideality factor. The recombination current \( J_0 \) is calculated through the principle of detailed balance: \( J_0 = \frac{1}{n} \int_0^\infty \frac{dE}{E} \cdot \frac{dE}{E} \cdot \phi_{BB,300K}(E) \cdot dE \). Here \( \phi_{BB,300K}(E) \) is the blackbody photon flux at 300K, and \( E Q E_{PV}(E) \) is the absorptance calculated from the transfer matrix calculation. The following diode parameters were assumed for the Cu₂AgBiI₆ sub-cell:¹⁴ \( R_{\text{shunt}} = 5 \, k\Omega \cdot \text{cm}^2 \), \( R_{\text{series}} = 4.2 \, \Omega \cdot \text{cm}^2 \), \( n = 1.0 \), \( E Q E_{EL} = 0.01 \). The calculated JV parameters for the Cu₂AgBiI₆ sub-cell were: \( \text{PCE} = 18.1\% \), \( V_{oc} = 1.16 \, \text{V} \), \( J_{sc} = 19.0 \, \text{mA/cm}^2 \), \( FF = 0.82 \). The following were
assumed for the Si sub-cell: \( R_{\text{shunt,SI}} = 10 \, k\Omega \cdot \text{cm}^2 \), \( R_{\text{Series,SI}} = 0.4 \, \Omega \cdot \text{cm}^2 \), \( n_{\text{SI}} = 1.04 \), \( EQE_{\text{EL,SI}} = 0.0056 \). The calculated \( JV \) parameters for the Silicon sub-cell were: PCE = 12.1\%, \( V_{\text{OC}} = 0.75 \) V, \( J_{\text{SC}} = 19.0 \) mA/cm\(^2\), \( FF = 0.84 \). The thickness of the LiF (20-200nm) the two ITO layers (20-200nm), and \( Cu_2AgBiI_6 \) (1200–1800nm) were varied with the indicated bounds using a differential evolution algorithm till a PCE maximum was obtained. The stack used as input for the Transfer Matrix Calculations is given in Table S5. The source of optical constants for each layer are also cited. For \( Cu_2AgBiI_6 \), a “synthetic” absorption co-efficient was created by splicing a 74 meV tail (gradient 1/0.074 eV) between 1.0 eV–1.88 eV, extracted from the gradient of the absorption onset from the combined PDS and FTIR datasets, to the absorption co-efficient obtained from FTIR measurements. The absorption co-efficient was set to zero below 1.0 eV. This was then converted into the extinction coefficient (Figure S21) which was transformed into the refractive index using the Kramer’s Kronig relation: \( n(\lambda) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\kappa'(E)}{E^2 - E_0^2} \, dE' \). The described method assumes the following:

1. Transfer Matrix Model Limitation: Layer roughness is much smaller than the wavelength of light (~550nm).
2. The “synthetic” absorption coefficient created by appending a tail of energy 74 meV between 1.88-1.45 eV characterises the material well.
3. The same transport materials conventionally used for hybrid perovskites, C60/SnO\(_2\) and PolyTPD are used. This is a relatively minor assumption as most transport layers are thin and poorly absorbing in comparison to the absorber layer, so the precise transport layer does not matter.
4. The \( Cu_2AgBiI_6 \) sub-cell can be optimised to bring it to the same radiative efficiency (EQE\(_{EL} = 1\%\)) as a well-performing hybrid lead halide perovskite cell. The same shunt and series resistances (\( R_{\text{shunt}} = 5 \, k\Omega \cdot \text{cm}^2 \), \( R_{\text{Series}} = 4.2 \, \Omega \)) can also be achieved.

Density Functional Theory Calculations

All periodic density functional theory calculations were performed using version 5.4 of the VASP code\(^7\) with the projector augmented wave method to describe core electrons.\(^8\) The crystal structure prediction package ChemDASH\(^9\) was used to generate low energy ordered configurations of atoms within \((2a+b, a+2b, c)\) supercells of the disordered experimental structure. Four independent starting configurations were initially generated by randomly occupying the experimental mixed and partially occupied Bi, Ag and Cu sites within the cell. ChemDASH was then used to generate 249 further configurations from each starting configuration by swapping between Bi, Ag and vacancies on the octahedral sites, and Cu and vacancies on the tetrahedral sites. A basin hopping approach using a value for \( k_B T \) of 0.01 eV/atom for the Metropolis acceptance criterion was used to ensure that low energy configurations were generated. The geometry of each configuration was optimised using the optB86b-vdW functional\(^10\) to model the important van der Waals interactions between the large iodine anions within the structure. ChemDASH uses a multi-step approach to geometry optimisation, where the final step used here had a plane-wave energy cutoff of 500 eV and forces were minimised to below 0.02 eV/Å. The lowest energy configuration of the 249 generated starting from each of the four starting configurations were then taken forwards to calculate the electronic structure, giving four low energy configurations with significantly different Bi, Ag and Cu orderings. A more accurate geometry was obtained for each of these configurations by performing a further geometry optimisation with the optB86b-vdW functional but with a higher plane-wave energy cutoff of 550 eV and a denser \( k \)-point mesh with a \( k \)-point spacing of 0.1 Å\(^-1\) and to a tighter force threshold of 0.001 eV/Å for convergence (Figure S22). A single-point calculation using the SCAN meta-GGA functional\(^11\) and including the effects of spin-orbit coupling was then used to compute the electronic structure of each of these four configurations, resulting in the partial density of states plots shown in Figure S3c and Figure S13. Band structure diagrams in Figure S14 for the lowest energy computed structure of \( Cu_2AgBiI_6 \) utilise the SCAN functional and including spin-orbit coupling effects.
Figure S1. (a) The TEM EDX of particles from the Cu$_2$AgBiI$_6$ powder synthesis, showing how quenching from 350°C, rather than cooling slowly to room temperature, gives a compositionally homogeneous sample. (b) The samples are also more compositionally homogeneous if the melt is avoided.
Figure S2. (a) The SEM image of the Cu₂AgBiI₆ crystal used for the SCXRD structural solution. The crystal was picked out of the Cu₂AgBiI₆ powder synthesis. (b) The SEM EDX showing the composition of the crystal to be within error of the powder.
Figure S3. (a) The trigonal unit cell and cubic close packed (CCP) iodide sub-lattice of Cu$_2$AgBiI$_6$. (b) The quantitative definition of rhombohedral strain used here, as well as the visualisation of the relationship between a metrically cubic trigonal cell ($R\bar{3}m$) and a cubic unit cell ($Fd\bar{3}m$). (c) The octahedral motif of Cu$_2$AgBiI$_6$ (the CdCl$_2$ structure). The number of octahedral sites occupied is $\frac{1}{2}$ of the total allowed by the structure (due to the vacant layers), however in Cu$_2$AgBiI$_6$, the atomic occupancies of these sites are less than one (disordered). (d) The two tetrahedral sites of Cu$_2$AgBiI$_6$. Site Cu1 is found in the layers containing octahedral occupancy, and site Cu2 is found in the layers without octahedral occupancy. In Cu$_2$AgBiI$_6$, these Cu sites are not fully occupied (disordered) but do show layered ordering and therefore can be described as possessing partial layered ordering.
Figure S4. The Pawley fit to room temperature laboratory PXRD data of CuBiI₄. The PXRD pattern is fitted using a cubic unit cell with space group Fd\(\bar{3}m\), previously reported by Fourcroy et al.\textsuperscript{22} The extracted lattice parameter is \(a = 12.1580(2)\ \text{Å}\).
Figure S5. SEM EDX of the powder corresponding to nominal composition $x = 0 \text{Cu}_{1.3\pm 3}\text{Bi}_{1.1\pm 4}\text{I}_{4.0\pm 9}$, giving an average composition of $\text{Cu}_{1.21(5)}\text{Bi}_{1.11(7)}\text{I}_{4.00(9)}$, and referred to as CuBiI₄ throughout the text.
Figure S6. The PXRD patterns of (a) CuBiI₄ as synthesised (b) CuBiI₄ kept in the dark in air at room temperature for three weeks, and (c) CuBiI₄ kept in the dark at -20° C for three weeks. The main peak of the BiI₃ decomposition phase is marked by the asterisk.
Figure S7. The PXRD patterns of AgBiI₄ and Cu₂AgBiI₆ powders after being exposed to one week in the solar spectrum, sealed in capillaries in air. Also shown are the PXRD of the controls, which were kept in the dark in air. The range shown includes where the largest peaks would appear for possible decomposition phases AgI (black tick marks), CuI (red tick marks) and BiI₃ (blue tick marks), should they have been present.
Figure S8. (a) The Raman spectra of AgBiI$_4$ and Cu$_2$AgBiI$_6$ control samples, showing the characteristic two peaks, which occur at low wavenumbers. The Raman spectra of AgBiI$_4$ and Cu$_2$AgBiI$_6$ powders after being exposed to the AM1.5 solar spectrum in different atmospheres are shown in b and c, respectively. There are no significant changes in the spectra of either materials. The change in ratio of the two peaks in the AgBiI$_4$ He 1 week spectra is likely due to the disorder of the Ag$^+$ and Bi$^{3+}$ cations.
**Figure S9.** Pawley fit of PXRD pattern for Cu$_2$AgBiI$_6$ films spincoated on FTO glass, fitted to a rhombohedral phase associated with a quaternary phase (black tick marks), a rhombohedral phase consistent with a Cu$_{3x}$Bi$_{1-x}$I$_3$ phase (red tick marks), and SnO$_2$ (blue tick marks).
Figure S10. SEM images of (a, b) rough, large, dendritic grains obtained during the early stages of solution processing the Cu$_2$AgBiI$_6$ films.
Figure S11. (a, b) SEM images of the uniform, smooth morphology of the optimised Cu$_2$AgBiI$_6$ film at x1001 and x13362 magnification, respectively.
Figure S12. (a) The raw PDS data of Cu$_2$AgBiI$_6$ thin films. (b) The PDS data (red) is scaled to match the absorption coefficient measured by FTIR (black).
Figure S13. The partial density of states plots for the lowest energy configurations arising from each of the four independent ChemDASH calculations shown in Figure S22. The electronic structure is computed using the meta-GGA functional, SCAN, and including spin-orbit coupling. Shown on each plot is the value of the smallest gap between occupied and unoccupied bands. The plot for configuration 1, the lowest energy configuration overall is also shown in Figure 3c of the main text, but is included again here for comparison. Although changing the configuration of Ag\(^{+}\), Bi\(^{3+}\) and Cu\(^{+}\) cations within the computed cell does affect the position and shape of peaks in the density of states, in all configurations the Cu 3d-states dominate at the valence band edge, and the conduction band consists of mixed Bi 6p-states and I 5p-states.
Figure S14. Band structure diagrams for the lowest energy computed structure of Cu$_2$AgBiI$_6$ (Figure S22) using the SCAN functional and including spin-orbit coupling effects. a)-c) Show the band dispersion around the conduction band maximum in the $k_x$, $k_y$ and $k_z$ directions and the effective mass of electrons derived from these. d)-f) Show the band dispersion around the valence band maximum in the $k_x$, $k_y$ and $k_z$ directions and the effective mass of holes derived from these.
Figure S15. The reported photoluminescence (red) and absorption coefficient (black) of MAPbI$_3$ thin films, reproduced from Wright et al. and Davies et al. respectively. 8-9
Figure S16. (a) The natural logarithm of the absorption coefficient measured by Photothermal Deflection Spectroscopy (PDS), after it was scaled to match the FTIR absorption coefficient data (raw data and scaled data shown in Figures S12a and b, respectively), showing sub-band gap states down to 1.25 eV. (b) Transient photoluminescence measurement on Cu$_2$AgBiI$_6$ (red) fitted by a stretched exponential function (black) with an average lifetime of 33 ns, compared to that of Cs$_2$AgBiBr$_6$ (blue) with an average lifetime of 10 ns, reproduced from Longo et al. The Cu$_2$AgBiI$_6$ and Cs$_2$AgBiBr$_6$ films were measured at excitation fluences of 200 nJ cm$^{-2}$ and 240 nJ cm$^{-2}$, respectively.
Figure S17. (a) The structure of the cell in the optical modelling LiF/ITO/SnO$_2$/C60/Cu$_2$AgBiI$_6$/PolyTPD/ITO/nc-SiO$_2$/(i)a-Si:H/(i)a-Si:H/(p)a-Si:H/AZO/Ag. (b) The photovoltaic (PV) band gap, defined as the energy of the inflection point on the absorption edge, for Cu$_2$AgBiI$_6$ films of varying thicknesses. (c) The external quantum efficiency (EQE) and (d) the J-V curve of a simulated Cu$_2$AgBiI$_6$ on c-Si tandem solar cell, using a transfer matrix optical model, coupled with detailed balance. The diode parameters used were extracted from lead halide perovskite and c-Si J-V curves reported in literature (see SI for more details).
Figure S18. The external quantum efficiencies (EQE) (left) and the J-V curves (right) of simulated Cu₂AgBiI₆ films of varying thickness on c-Si tandem cells, using a transfer matrix optical model, coupled with detailed balance. The diode parameters used were extracted from lead halide perovskite and c-Si J-V curves reported in literature (see SI for more details). The search bounds for Cu₂AgBiI₆ film thicknesses were 1200–1400 nm, 800–1000 nm, and 400–530 nm for the films that optimised at thicknesses of 1389 nm, 999.9 nm and 529.6 nm, respectively. LiF film thickness optimised at 97.3 nm, 96.8 nm, 95.3 nm for the 1389 nm, 999.9 nm and 529.6 nm Cu₂AgBiI₆ film thicknesses, respectively.
The optical response of a Cs$_2$AgBiBr$_6$ on silicon tandem was modelled using the transfer matrix method. The thickness of the Cs$_2$AgBiBr$_6$ (100 nm – 1000 nm) and the anti-reflective coating LiF (10nm – 150 nm) was varied using a differential evolution algorithm till the limiting tandem current was maximised. The optimised device structure was LiF (110 nm)/ITO (80 nm)/SnO$_2$ (5 nm)/C60 (10 nm)/Cs$_2$AgBiBr$_6$ (989 nm)/PolyTPD (5 nm)/ITO (25 nm)/nc-SiO$_x$:H (110 nm)/i-a-Si:H (5 nm)/i-c-Si (250 um)/i-a-Si:H (5 nm)/p-a-Si:H (5 nm)/AZO (70 nm)/Ag (400 nm). The c-Si sub-cell (32.9 mA/cm$^2$) generates six times as much as current as the Cs$_2$AgBiBr$_6$ cell (5.5 mA/cm$^2$). This huge current mismatch makes Cs$_2$AgBiBr$_6$ impractical as the top cell of a Si based tandem.
Figure S20. PXRD patterns for the compositional screening of Cu$_{3x}$Bi$_1$I$_3$ carried out between 0.18 ≤ $x$ ≤ 0.32. A pure CuBiI$_4$ powder was obtained for the nominal composition corresponding to $x$ = 0.25. For values of $x$ < 0.25 BiI$_3$ impurities were seen (black asterisks). For values of $x$ > 0.25 small amounts of CuI impurities were seen which appear on the shoulders of the CuBiI$_4$ peaks (red asterisks). The expanded view of the peak at 1.8 Å$^{-1}$ in the PXRD patterns of $x$ > 0.25, shows the amount of CuI increases with increasing $x$ above 0.25.
Figure S21. The “synthetic” extinction co-efficient for Cu$_2$AgBiI$_6$ which was used as input for the optical calculations, as described in the optical modelling.
Figure S22. The optimised geometry of the lowest energy configurations arising from each of the four independent ChemDASH calculations computed using the van der Waals functional, optB86b-vdW.\textsuperscript{20} The computed energy for each configuration is given relative to configuration 1, the lowest energy overall. The green, blue, grey and pink spheres/polyhedra represent I\textsuperscript{−}, Cu\textsuperscript{+}, Ag\textsuperscript{+} and Bi\textsuperscript{3+} ions respectively. These low energy configurations represent different ordered arrangements of the cations consistent with the average structure determined experimentally.
Table S1. The twinning matrix and contribution of each twin indexing the Cu$_2$AgBiI$_6$ 100K SCXRD data with a 4-fold twin of smaller trigonal unit cells.

| Twin 1 | Refined mass fraction (%) | 24.9(1.2) | Isolated reflections | 728 | Overlapped reflections |
|--------|--------------------------|-----------|---------------------|-----|-----------------------|
|        |                          |           |                     |     | Twin matrix            |
|        |                          |           |                     |     | [1 0 0]                |
|        |                          |           |                     |     | [0 1 0]                |
|        |                          |           |                     |     | [0 0 1]                |

| Twin 2 | Refined mass fraction (%) | 25.2(7)  | Isolated reflections | 729 | Overlapped reflections |
|--------|--------------------------|----------|---------------------|-----|-----------------------|
|        |                          |          |                     |     | Twin matrix            |
|        |                          |          |                     |     | [−0.3335 −0.6669 −0.1666] |
|        |                          |          |                     |     | [1.0003 1.0005 −0.0001] |
|        |                          |          |                     |     | [2.6652 −2.6675 0.3338] |

| Twin 3 | Refined mass fraction (%) | 25.0(7)  | Isolated reflections | 729 | Overlapped reflections |
|--------|--------------------------|----------|---------------------|-----|-----------------------|
|        |                          |          |                     |     | Twin matrix            |
|        |                          |          |                     |     | [−0.6662 −0.3332 0.1667] |
|        |                          |          |                     |     | [−0.3340 −0.6671 −0.1667] |
|        |                          |          |                     |     | [2.6660 −2.6665 0.3331] |

| Twin 4 | Refined mass fraction (%) | 24.9(7)  | Isolated reflections | 745 | Overlapped reflections |
|--------|--------------------------|----------|---------------------|-----|-----------------------|
|        |                          |          |                     |     | Twin matrix            |
|        |                          |          |                     |     | [0.9982 0.9973 −0.0001] |
|        |                          |          |                     |     | [−0.6647 −0.3313 0.1663] |
|        |                          |          |                     |     | [2.6594 −2.6646 0.3327] |


Table S2. Cu$_2$AgBiI$_6$ structural refinement of single crystal X-ray data collected at 100 K.

| Identification code       | Cu$_2$AgBiI$_6$ _SCXRD_100K |
|---------------------------|------------------------------|
| Empirical formula         | Cu$_{2.15}$Ag$_{1.04}$Bi$_{0.92}$I$_{6.00}$ |
| Formula weight            | 1202.46                      |
| Temperature (K)           | 100(2)                       |
| Crystal system            | trigonal                     |
| Space group               | $R3m$                        |
| a (Å)                     | 4.2749(3)                    |
| c (Å)                     | 20.9395(16)                  |
| Volume (Å$^3$)            | 331.40(5)                    |
| Z                         | 1.19988                      |
| $\rho_{\text{calc}}$ (g/cm$^3$) | 6.025                       |
| $\mu$ (mm$^{-1}$)        | 31.009                       |
| F(000)                    | 506.0                        |
| Crystal size (mm)         | 0.02 × 0.03 × 0.01           |
| Radiation                 | MoKα ($\lambda = 0.71073$)  |
| 2θ range for data collection (°) | 5.836 to 55.51             |
| Index ranges              | -5 ≤ h ≤ 5, -5 ≤ k ≤ 5, -26 ≤ l ≤ 27 |
| Reflections collected     | 501                          |
| Independent reflections   | 501 [R$_{\text{sigma}}$ = 0.0204] |
| Data/restraints/parameters| 501/0/12                     |
| Goodness-of-fit on $F^2$  | 1.130                        |
| Final R indexes [I ≥ 2σ]  | $R_1 = 0.0441$, $wR_2 = 0.1024$ |
| Final R indexes [all data]| $R_1 = 0.0495$, $wR_2 = 0.1053$ |
| Largest diff. peak/hole (eÅ$^3$) | 2.95/-4.31             |
**Table S3.** Bond distances and bond angles for the Cu$_2$AgBi$_6$ structure refined against 100K SCXRD data.

| Bond distances (Å) | Bond angles (°) |
|--------------------|-----------------|
| **Cu$_2$AgBi$_6$ 100K SCXRD** | **i-CdCl$_2$** |
| Oct1 I1 3.0471(9) | I1 Oct1 I1 89.09(4) |
| Cu1 I1 2.81(4)   | I1 Oct1 I1 90.91(4) |
| Cu1 I1 2.583(12) | I1 Cu1 I1 107.1(9) |
| Cu2 I1 2.73(4)   | I1 Cu1 I1 111.7(8) |
| Cu2 I1 2.558(11) | I1 Cu2 I1 105.2(9) |
| I1 I1 4.206(3)   | I1 Cu2 I1 113.3(8) |
| I1 I1 4.2749(3)  | I1 I1 I1 58.96(4) |
| I1 I1 4.343(3)   | I1 I1 I1 59.46(2) |
|                   | I1 I1 I1 60.519(19) |
|                   | I1 I1 I1 60.000(5) |
**Table S4.** Relative errors of the 1σ standard deviation in the measured compositions obtained by SEM and TEM EDX. CuI and AgI were purchased, the remaining were synthesised.

| Sample, measurement technique | Relative 1σ error in measured composition (%) |
|------------------------------|---------------------------------------------|
|                              | Cu  | Ag  | Bi  | I   |
| CuI (SEM EDX)               | 3   |     |     | 2   |
| AgI (SEM EDX)               |     | 2   |     | 2   |
| BiI₃ (SEM EDX)              |     |     | 4   | 2   |
| CuBiI₄ (SEM EDX)            | 4   | 6   | 2   |
| CuI (TEM EDX)               | 3   |     |     | 3   |
| AgI (TEM EDX)               |     | 2   |     | 2   |
| BiI₃ (TEM EDX)              |     |     | 5   | 2   |
| Cu₂AgBiI₆ powder (TEM EDX)  | 7   | 5   | 8   | 2   |
| Cu₂AgBiI₆ film (TEM EDX)    | 4   | 7   | 13  | 3   |
Table S5. The stack used as input for the Transfer Matrix Calculations

| Layer                  | Thickness  |
|-----------------------|------------|
| LiF                   | 110 nm     |
| ITO\textsuperscript{24} | 80 nm      |
| SnO\textsubscript{2}\textsuperscript{25} | 5 nm       |
| C60\textsuperscript{26} | 10 nm      |
| Cu\textsubscript{2}AgBiI\textsubscript{6} | 1710 nm    |
| PolyTPD\textsuperscript{27} | 5 nm       |
| ITO\textsuperscript{24} | 25 nm      |
| Nc-SiO\textsubscript{x}:H\textsuperscript{24} | 110 nm     |
| (i)a-Si:H\textsuperscript{28} | 5 nm       |
| c-Si\textsuperscript{29} | 250 μm     |
| (i)a-Si:H\textsuperscript{28} | 5 nm       |
| (p)a-Si:H\textsuperscript{28} | 5 nm       |
| AZO\textsuperscript{30} | 70 nm      |
| Ag\textsuperscript{31} | 400 nm     |
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