Near-Infrared Light-Responsive Cu-Doped Cs₂AgBiBr₆

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Lead-free halide double perovskites (A₂Bᴵᴵᴵ𝑋₆) with attractive optical and electronic features are considered to be a promising candidate to overcome the toxicity and stability issues of lead halide perovskites (APbX₂). However, their poor absorption profiles limit device performance. Here the absorption band edge of Cs₂AgBiBr₆ double perovskite to the near-infrared range is significantly broadened by developing doped double perovskites, Cs₂(Ag:Cu)BiBr₆. The partial replacement of Ag ions by Cu ions in the crystal lattice is confirmed by X-ray photoelectron spectroscopy (XPS) and solid-state nuclear magnetic resonance (ssNMR) measurements. Cu doping barely affects the bandgap of Cs₂AgBiBr₆; instead it introduces subbandgap states with strong absorption to the near-infrared range. More interestingly, the near-infrared absorption can generate band carriers upon excitation, as indicated by the photoconductivity measurement. This work sheds new light on the absorption modulation of halide double perovskites for future efficient optoelectronic devices.

1. Introduction

Metal halide perovskites have rapidly advanced in the optoelectronic field due to their suitable bandgaps, long carrier diffusion length, exceptional defect tolerance, and low-cost solution processing.[1–4] However, the best-performing perovskites contain toxic lead (Pb) and are also inferior to commercial devices in terms of stability.[5] Recently, there has been a wide range of low-toxic/nontoxic and stable lead-free optoelectronic perovskites/perovskite derivatives reported, including 3D A₂BᴵᴵᴵCl₂X₆,[6,7] 2D A₁Bᴵᴵᴵ₂X₉,[8] 0D A₁Bᴵᴵ⁺X₂[9] and 0D A₁B⁺X₂[9] (A = Cs⁺, MA⁺, FA⁺; B = metal ions; X = Cl⁻, Br⁻, I⁻). Unfortunately, most of these lead-free perovskites and perovskite derivatives show low device efficiency due to their intrinsic deficiencies, including low electronic dimensionality, large bandgaps, large hole effective mass, and poor carrier transport.[11,12] Among others, 3D double perovskites (A₂BᴵᴵᴵCl₂X₆) have been considered as the most promising lead-free perovskite system. Lead-free halide double perovskites (e.g., Cs₂AgBiBr₆) demonstrate diverse electronic structures,[13] optical responses,[14] and superior material stability.[15] The key challenge with them is limited absorption (below 650 nm). Therefore, it is highly desirable to find efficient strategies to extend their absorption, making it possible to develop high-efficiency optoelectronic devices based on these double perovskites.

Efficient impurity doping/alloying is a primary method to improve the absorption of traditional semiconductors. There have been several attempts to dope the benchmark double perovskite Cs₂AgBiBr₆, aiming to extend their absorption. For example, Slavney and co-workers successfully extended the absorption of Cs₂AgBiBr₆ to ≈886 nm through Tl-doping; however, Tl also suffers from toxicity issue.[16] Mitzi and co-workers tuned the absorption of Cs₂AgBiBr₆ by trivalent Sb-doping, resulting in the absorption edge broadening from ≈585 to ≈667 nm, which needs to be further extended.[17] Apart from isovalent (mono-, trivalent-) doping, heterovalent doping (e.g., bivalent Sn²⁺) has also been tried to tune the absorption features in Cs₂AgBiBr₆ crystals. Unfortunately, Sn readily oxidizes, making the doped perovskites highly sensitive to the ambient atmosphere.[18] Therefore, finding rational doping/alloying metal ions to significantly modify the absorption features of double perovskites is still challenging.

In this work, we use the benchmark photovoltaic double perovskite Cs₂AgBiBr₆ as a host material, and achieve new modified double perovskites Cs₂(Ag:Cu)BiBr₆ through Cu doping. The absorption edges of Cs₂AgBiBr₆ can be significantly broadened to the near-infrared range (NIR) after Cu-doping, as a result of strong absorption from sub-bandgap states. The XPS and ssNMR measurements indicate that both Cu⁺ and Cu²⁺ are

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doped into Cs2(Ag:Cu)BiBr6 crystals by replacing the position of Ag⁺. First-principles electronic structure calculations indicate that the Cu doping very weakly affects the valence and conduction bands of the host. The photoconductivity measurements confirm the generation of band carriers with below bandgap excitation, implying a great potential application in NIR photodetector and other optoelectronics devices.

2. Results and Discussion

High-quality, large-size Cu-doped Cs2AgBiBr6 single crystals with the octahedral shape are obtained by the hydrothermal method (Figure 1a). The doping level of Cu is tuned by different amounts of CuBr₂ (Cu%) in the precursor solution. Detailed synthesis procedures are provided in the Supporting Information. We name the resulting crystal samples by the molar ratio of Cu ions relative to that of Ag in the precursor solutions (Cu-0, Cu-1, Cu-10, Cu-30, and Cu-50). We note that the molar ratio of the remaining Cu in the resulting crystals could be significantly different from that in the precursors, and hence use the inductively coupled plasma mass spectrometry (ICP-MS) measurement to determine the value. The result indicates that the molar ratio of Cu to Ag is only ≈1% (mol%) in the Cu-50 sample (Table S1, Supporting Information). In spite of the small amount of Cu-doping, we observe obvious color changes from red to black with increasing Cu-concentration (Figure 1a). We perform a range of structural and spectroscopic measurements to understand the Cu doping and how it affects the crystal colors.

The powder X-ray diffraction (XRD) measurements indicate that Cu-doping does not change the crystal structures of samples. As shown in Figure 1b, all diffraction patterns of Cu-doped samples are similar to pristine Cs2AgBiBr6 (Cu-0), indicating their high phase purity and cubic structures. Meanwhile, the (400) peak in Cu-50 shifts slightly towards the high angle side compared to Cu-0, suggesting the lattice shrink after Cu doping (Figure S1 and Table S2, Supporting Information). This phenomenon can be understood by the fact that the ionic radii of Cu ions (Cu⁺ (0.77 Å)/Cu²⁺ (0.73 Å)) are smaller compared with those for Ag⁺ (1.15 Å) and Bi³⁺ (1.03 Å). Considering that Cu ions exhibit multiple valence states (stable as +1, +2) in compounds, which are possibly formed through rich redox reactions during the synthesis, we perform the XPS measurement to investigate the valence state of Cu. As shown in Figure 1c, the weak Cu 2p3/2 signal at 932 eV indicates that Cu⁺ is the main state of Cu in the doped crystals. The core levels of Cs 3d, Ag 3d, Bi 4f, and Br 3d in full XPS spectra are consistent with those of previous reports (Figure S2, Supporting Information).

To understand the exact position of Cu ions in the lattice, and to gain deep insight into the structure of pristine and Cu-doped Cs2AgBiBr6, we perform ¹³³Cs, ²⁰⁹Bi solid-state NMR (MAS ssNMR) experiments. As shown in Figure 2a, only one symmetric peak locating at δiso = 80.7 ± 0.5 ppm is observed in the ¹³³Cs MAS NMR spectra, confirming the existence of one crystallographic position of the Cs⁺ ions in Cu-0. In contrast, for Cu-50, two signals are observed in the ¹³³Cs MAS NMR spectra, first remaining at δiso = 80.7 ± 0.5 ppm and a new smaller peak appearing at δiso = 83.4 ± 0.5 ppm (Figure 2b). The second signal (δiso = 83.4 ppm) implies the presence of Cu ions, most probably both Cu⁺/Cu²⁺, close to Cs⁺ ions.[21,22] In general, the presence of paramagnetic metal centers (e.g., Cu⁺) usually cause extremely rapid longitudinal and transverse relaxation of the nearby nuclei due to electron spin couplings. So, we further perform ¹³³Cs spin-lattice T₁-relaxation measurements on pristine and Cu-doped Cs₂AgBiBr₆ (Figure S3, Supporting Information).[23] Resulting relaxation times and roughly estimated amounts of individual phases are summarized in

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**Figure 1.** Optical images a) and PXRD patterns b) of pristine Cs₂AgBiBr₆ (Cu-0) and Cu-doped Cs₂AgBiBr₆ (Cu-1, Cu-10, Cu-30, Cu-50). c) XPS Cu 2p3/2 spectrum of the Cu-50 crystal.
Table S3 (Supporting Information). We detected a slow $T_1$ relaxation time of 306 s in Cu-0 and one slow- and one fast-relaxing phase corresponding to signals at $\delta_{iso} = 80.7 \pm 0.5$ ppm (103 s) and $\delta_{iso} = 83.4 \pm 0.5$ ppm (2 s) in Cu-50. Very small amount of rapidly relaxed phase/signal and lower shortening of relaxation time of signal corresponding to Cu-0 in case of Cu-50 would imply the presence of trace paramagnetic ions (e.g., Cu$^{2+}$) distributed in the Cu-50 framework.

By further analyzing the $^{209}$Bi ssNMR spectra of the Cu-0 and Cu-50 (Figure 2c,d), a very broad (few hundred ppm) signal at $\delta_{iso} = 5500$ ppm is detected in Cu-50 (Figure 2d). The significant signal broadening of Cu-50 further confirms the existence of Cu ions in the lattice. Another useful probe to the local bonding environment is provided by the presence and magnitude of spin–spin interaction (J-coupling).\cite{24} The spin–spin interaction ($J_X$$_{Bi}$ = 1341 Hz, where $X$ can be Br, Ag or Cu) in Cu-50 is significantly different from that in Cu-0 ($J_X$$_{Bi}$ = 2002 Hz, where $X$ can be either Br or Ag), suggesting a different environment of Bi atoms caused by the replacement of Ag atoms by Cu$^{+}$/Cu$^{2+}$ ions. Based on this understanding, we name the Cu-doped Cs$_2$AgBiBr$_6$ samples as Cs$_2$(Ag:Cu)BiBr$_6$ in the following parts.

Considering the different valence states of Cu$^{2+}$ and Ag$^{+}$ ions, the substitution would possibly produce a neighboring cation vacancy (like Ag$^{+}$ vacancies) to maintain charge balance neutrality of the doped materials.\cite{21}

We then perform UV–vis absorbance and photoluminescence (PL) measurements to understand the optical properties of samples. As shown in Figure 3a, UV–vis spectra indicate that spin-spin interaction (J-coupling).\cite{24} The spin–spin interaction ($J_X$$_{Bi}$ = 1341 Hz, where $X$ can be Br, Ag or Cu) in Cu-50 is significantly different from that in Cu-0 ($J_X$$_{Bi}$ = 2002 Hz, where $X$ can be either Br or Ag), suggesting a different environment of Bi atoms caused by the replacement of Ag atoms by Cu$^{+}$/Cu$^{2+}$ ions. Based on this understanding, we name the Cu-doped Cs$_2$AgBiBr$_6$ samples as Cs$_2$(Ag:Cu)BiBr$_6$ in the following parts.

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pristine Cs$_2$AgBiBr$_6$ (Cu-0) shows a sharp absorption edge at \( \approx 610 \) nm, similar to previous reports. After introducing Cu dopants, a new tail absorption edge at \( \approx 860 \) nm (NIR range) is observed. The increased intensity of NIR absorption with increasing amount of Cu dopant agrees with the observed crystal color change in Figure 1a. PL spectra show that the Cs$_2$(Ag:Cu)BiBr$_6$ double perovskites exhibit a broad peak at \( \approx 660 \) nm (Figure 3b), similar to pristine Cs$_2$AgBiBr$_6$. Meanwhile, the PL intensities of the doped samples are much lower than that of the pristine one (Figure S4, Supporting Information). We further perform the time-resolved photoluminescence (TRPL) for all samples at room temperature, and Cs$_2$(Ag:Cu)BiBr$_6$ single crystals show shorter PL lifetime than pristine Cs$_2$AgBiBr$_6$ (Figure S5, Supporting Information). These results imply that the bandgap of Cs$_2$AgBiBr$_6$ is hardly changed; instead, defect states are introduced after Cu doping. Therefore, the tail NIR state absorption after Cu-doping is related to introduced defect states (sub-bandgap states). These experimental results are consistent with our first-principles density functional theory (DFT) calculations, see SI for details. The calculations reveal that the direct effects of Cu$^+$ replacement are small, in particular, the effect on the bandgap is negligible. This is in full agreement with our experimental indications of essentially unchanged bandgap and the observed NIR absorption in the Cu doped samples is due to induced defect states, and not a direct effect of Cu on the electronic structure.

Motivated by the strong absorption from the sub-bandgap states, we carry out photocurrent measurements on Cs$_2$AgBiBr$_6$ and Cs$_2$(Ag:Cu)BiBr$_6$ single crystals to understand whether these states are photoactive and potentially useful for optoelectronic devices (Figure 4a). Photogeneration of carriers can occur both via the band-to-band transition and via a transition between a defect level and either the valence or conduction band, see Figure 4b where a transition between a defect level and the valence band is shown as an example. \( \Delta G \) is known to be proportional to \( \Delta G \propto q(\Delta n\mu_e + \Delta p\mu_h) + q\Delta p\mu_h \), where the first term concerns the band-to-band transition that only applies to above bandgap excitation whereas the second term involves the defect that is active under both below and above bandgap excitation. \( \Delta n \) and \( \Delta p \) (or \( \Delta p' \)) refer to the densities of photogenerated electrons in the conduction band and holes in the valence band, respectively. \( \mu_e \) and \( \mu_h \) are the electron and hole mobility. In Figure 4c, we show the \( \Delta G \) spectra of the two devices as a function the excitation photon energy, in which both spectra are normalized to their maximum at around 2.25 eV, right above the bandgap energy \( E_g \). Such approach ensures that the above bandgap excitation would generate a comparable photocurrent regardless of changes in lifetime, mobility etc. at different doping levels. A sharp rise of \( \Delta G \) with photon energy increasing from \( E_g \) marks the onset of the intrinsic photocconductivity with the band edge absorption in both samples. With further increase of the excitation photon energy above the bandgap, the light penetration-depth is expected to reduce and carriers are predominately generated at the sample surface where mobility, carrier lifetime, etc. rapidly deteriorate due to surface effect. This probably explains the observed decrease of \( \Delta G \) at a photon energy above 2.3 eV in both samples.

Moving to the near infrared spectral range, while it is absent in the pristine Cs$_2$AgBiBr$_6$, a strong photoc conductivity contribution from the sub-bandgap absorption is found in the Cs$_2$(Ag:Cu)BiBr$_6$ (Cu-50) sample. The sub-bandgap photocconductivity rises when photon energy is above the threshold energy \( E_T = 1.3 \) eV, which is comparable to the one found in the absorption spectra shown in Figure 3a. It is associated with an optical transition between the valence (or conduction) band and a deep-level defect state that is located at around 1.3 eV above the valence band as illustrated in Figure 4b (or below the conduction band). We note that deep level related absorption has been observed and utilized for light detection in other semiconductor materials. In most cases in semiconductors, however, \( \Delta G \) is expected to be much smaller for sub-bandgap excitation as compared to the band-to-band (BB) excitation due to usually small density of defect states and

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Figure 4. a) Schematic diagram of the photocurrent measurements. b) Schematic illustration of photo-excitation processes in Cs$_2$(Ag:Cu)BiBr$_6$ perovskites. c) The photocconductance spectra of the Cs$_2$AgBiBr$_6$ (Cu-0) and Cs$_2$(Ag:Cu)BiBr$_6$ (Cu-50) single crystals at room temperature.
optical cross section for defect-to-band (DB) absorption. What is noticeable here is that the subbandgap photocconductivity contributed by the defect-to-band (DB) absorption almost rises up to a comparable level as the band-to-band (BB) contribution. The noticeable subbandgap photocconductivity measured from the Cs$_2$(Ag:Cu)BiBr$_6$ is the direct consequence of relatively strong sub-bandgap absorption which is evident in the absorption spectra in Figure 3a, suggesting appreciable photocarrier generation via DB absorption. This is, on the other hand, due to indirect nature of the Cs$_2$AgBiBr$_6$, whose near-band-edge BB transition requires the assistance of phonon and is deemed to be weaker than typical direct bandgap semiconductor. On the other hand, the 1% Cu incorporation corresponding to a concentration of $2.8 \times 10^{19}$ cm$^{-3}$, though negligible for any alloying effect, is considered to be high enough for defects or dopants in a semiconductor. For instance, in Si at the doping concentration of $7 \times 10^{17}$ cm$^{-3}$, the high density deep level defects forms an additional band inside the bandgap, which has the implementation for the application as intermediate band solar cell.\cite{28,29} The prominent subbandgap absorption and photocconductivity thus suggests a great potential for using such devices for near-infrared light detection.

3. Conclusion

We have successfully synthesized new double perovskites Cs$_2$(Ag:Cu)BiBr$_6$ with enhanced NIR absorption through Cu-doping. The NIR absorption intensity is proportional to the doping amounts of Cu ions efficiently. The XPS and ssNMR results indicate both Cu$^+$ and Cu$^{2+}$ are doped into the crystal lattice to replace the position of Ag$^+$. Both the UV–vis and PL spectrum, supported by the DFT calculations of the electronic spectrum, suggest that the implementation for the application as intermediate band solar cell (IBC) is promising. The prominent subbandgap absorption and photocconductivity thus suggests a great potential for using such devices for near-infrared light detection.

4. Experimental Section

**Chemicals and Materials:** All the chemicals used were purchased from Sigma-Aldrich without any further purification.

**Preparation of Pristine Cs$_2$AgBiBr$_6$ Crystals:** Solid CsBr (213 mg, 1.00 mmol), BiBr$_3$ (224 mg, 0.5 mmol) and AgBr (94 mg, 0.5 mmol) were dissolved in 6 mL of 48% HBr and then transferred into a 25 cm$^3$ Teflon-lined autoclave. The autoclave was sealed and placed in the oven where it was heated at 120 °C for 24 h. After being slowly cooled to room temperature at a rate of 1 °C h$^{-1}$, red octahedral single crystals were achieved.

**Preparation of Cu-Doped Cs$_2$AgBiBr$_6$ Crystals:** For Cu-doped Cs$_2$AgBiBr$_6$ crystals, x% (molar ratio) BiBr$_3$ is replaced by equimolar CuBr$_2$ with 1%, 10%, 30%, 50% in the precursor solutions, respectively. The synthesis approach is the same as that used for pristine Cs$_2$AgBiBr$_6$.

**Characterization:** The XRD patterns of the products were recorded with a X'Pert PRO X-ray diffractometer using Cu Kα1 irradiation ($λ = 1.5406$ Å). The UV–vis absorption spectra were measured with a PerkinElmer model Lambda 900. Both XRD and UV measurements were performed using powders obtained after grinding the single crystals.

Steady-state photoluminescence spectra were recorded with a 405 nm laser and an Andor spectrometer (Shamrock sr-303i-B, coupled to a Newton EMCCD detector). For time-resolved photoluminescence (TRPL) measurement, a laser (405 nm, 1 PS pulse width) was used as excitation source at 2 MHz repetition rate (EPL 405, Edinburgh Instruments). The laser was focused onto single crystals by an objective lens (N.A. = 0.7, spot size = 1 µm, Mitutoyo) with power density of 4.5 µJ/µm$^2$/pulse. PL of the sample was collected by the same objective lens and sent to an avalanche photo diode (time resolution ≤ 40 ps, ID Quantique) in a time-correlated single photon counting system (timing jitter = 3 ps, Quotools) with an instrument response function of ≤ 56 ps. Inducively coupled plasma mass spectrometry (ICP-MS) analysis of Cu-doped samples was performed by Agilent 7700. The samples were completely digested in aqua regia to detect the concentrations of Cs, Bi, and Cu. The same batch of samples was additionally digested in HNO$_3$ acid to further measure the concentration of Ag. X-ray photoelectron spectroscopy (XPS) spectra were acquired using an ESCALAB 250 (Thermo Fisher Scientific) with 200 W Mg Ka radiation in twin anode and the distance between X-ray gun and sample is about 1 cm.

**Solid-State Nuclear Magnetic Resonance Analysis:** The solid-state NMR spectra (ssNMR) were recorded at 11.7 T using a Bruker AVANCE III HD spectrometer. The 4 mm cross-polarization magic angle spinning (CP/MAS) probe was used for $^{133}$Cs and $^{209}$Bi experiments at Larmor frequencies of $\nu(133)$Cs = 65.611 MHz and $\nu(209)$Bi = 80.858 MHz, respectively. $^{133}$Cs MAS NMR experiments were collected at 10 kHz spinning frequency without 1 H decoupling. The recycle delay was 4 s for all ssNMR experiments. The $^{133}$Cs chemical shift was calibrated using solid CsCl ($^{133}$Cs: 228.1 ppm.)\cite{30} The pulse length was set to 2.4 µs at 100 W for maximal signal intensity. The $^{133}$Cs rotor-synchronized (1 loop) spin-echo MAS NMR experiments (90°-nR-180°-nR-acq.) were performed. The $^{133}$Cs,$^{133}$Cs correlation MAS NMR spectra were recorded using NOESY-type three-pulse sequence. Duration of the spin-exchange period between the second and third pulse was 10 µs. Spectral width in both frequency dimensions was rotor-synchronized to be 10 kHz. The indirect detection period $\tau$ consisted of 128 increments each made of 48 scans. The $^{209}$Bi chemical shift was calibrated using a saturated solution of Bi(NO$_3$)$_3$·5H$_2$O in concentrated HNO$_3$ ($^{209}$Bi: 0.0 ppm.)\cite{31} The pulse length was 9.0 µs at 100 W at maximal signal intensity. $^{209}$Bi NMR experiments were collected at static conditions using spin-echo NMR experiments (90°-r-180°-acq.).\cite{32} The delay between pulses was 20 µs. To compensate for frictional heating of the spinning samples, all NMR experiments were measured under active cooling. The sample temperature was maintained at 298 K and the temperature calibration was performed on Pb(NO$_3$)$_2$ using a calibration procedure described in the literature.\cite{33} Dried sample was packed into ZrO$_2$ rotors and subsequently stored at room temperature. All NMR spectra were processed using the Top Spin 3.5 p2 software package.

**Photoconductive Measurement:** The photoconductive measurements were carried out for both the pristine Cs$_2$AgBiBr$_6$ (Cu-0) and Cs$_2$(Ag:Cu)BiBr$_6$ (Cu-50) single crystal devices made by evaporating two gold electrodes onto their (011) surfaces. The distance between the electrodes is about 1 mm for both devices. The schematic of the photocurrent measurement is shown in Figure 4a where a wavelength-tunable optical parametric oscillator is used as excitation. The laser beam is focused between the electrodes. A bias voltage of $V_{bias}$ = 40 V is applied across both the device and a load resistance of 1 MΩ. The laser pulse has duration of 10 ns and repetition rate of 20 Hz. The voltage difference across the sample at the on and off period the laser pulse ($\Delta V$) is measured. The currents were considered as photoconductance $\Delta G = \frac{\Delta V}{V_{bias}}$. The voltage $V_{on}$ and $G$ is the voltage drop and conductance of the perovskite device in the dark. The measured $\Delta G$ is normalized to the pulse energy to yield the spectral dependence conductance for both samples. G is found to be about 2.04 × 10$^{-3}$ and 9.17 × 10$^{-2}$ μS for Cs$_2$AgBiBr$_6$ (Cu-0) and Cs$_2$(Ag:Cu)BiBr$_6$ (Cu-50) sample, respectively.
First-Principles Calculations: All density functional theory (DFT) calculations were performed in the framework of the projector augmented wave (PAW)[34] method, as implemented in the Vienna ab initio simulation package (VASP).[35–37] A cutoff energy of 400 eV was used for the plane wave expansion of the Kohn-Sham orbitals. The exchange-correlation energy was approximated using the PBEsol[38] and the hybrid HSE06[39] functionals, including spin orbit coupling (SOC). The same 240 atom supercell was used as in ref. [40]. The lattice constant was fixed at the relaxed PBEsol equilibrium value (11.18 Å) and internal coordinates were relaxed until the residual forces were <10−3 eV Å−1 with Γ-point sampling of the Brillouin zone (BZ) and a Gaussian smearing with a width of 0.05 eV, without SOC. Effective band structures (EBS) were obtained following the methodology described in refs. [41,42] as implemented in the BandUP code.[43,44] The Cs2(Ag:Cu)BiBr6 system was modeled by replacing one Ag atom by one Cu atom in the 240 atom supercell, approximately corresponding to a chemical formula of Cs$_2$Ag$_{0.96}$Cu$_{0.04}$BiBr$_6$. It is noted that this is a larger concentration of Cu than in our experimental samples. Figure S6a (Supporting Information) shows the electronic density of states (DOS) of Cs$_2$Ag$_{0.96}$Cu$_{0.04}$BiBr$_6$ from a HSE06+SOC calculation, with the Cu-d states located toward the top of the valence band. Figure S6b (Supporting Information) shows the effective band structure of Cs$_2$Ag$_{0.96}$Cu$_{0.04}$BiBr$_6$, which has been unfolded from the Brillouin Zone of the 240 atom supercell to the BZ of the primitive face-centered cubic (fcc) unit cell of the double perovskite structure, compared to the primitive band structure of Cs$_2$AgBiBr$_6$, which has been unfolded from the Brillouin Zone of the 240 atom supercell to the BZ of the primitive face-centered cubic (fcc) unit cell of the double perovskite structure. As expected, it is seen that the main influence of the Cu alloying on the band structure is located toward the top of the valence band. The perturbation of the EBS with respect to the primitive band structure is, however, very weak, and the valence band top, in particular, is sharp, and slightly shifted up with respect to the conduction band. This is in agreement with the fact that the direct influence of replacing Ag$^+$ with Cu$^+$ has a very weak explicit effect on the electronic structure of Cs$_2$AgBiBr$_6$, even at Cu$^+$ concentrations roughly four times larger than in our actual samples.

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.

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