Bandgap lowering in mixed alloys of Cs$_2$Ag(Sb$_x$Bi$_{1-x}$)Br$_6$ double perovskite thin films†‡

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Halide double perovskites have gained significant attention, owing to their composition of low-toxicity elements, stability in air and long charge-carrier lifetimes. However, most double perovskites, including Cs$_2$AgBiBr$_6$, have wide bandgaps, which limits photoconversion efficiencies. The bandgap can be reduced through alloying with Sb$_{3+}$, but Sb-rich alloys are difficult to synthesize due to the high formation energy of Cs$_2$AgSbBr$_6$, which itself has a wide bandgap. We develop a solution-based route to synthesize phase-pure Cs$_2$Ag(Sb$_x$Bi$_{1-x}$)Br$_6$ thin films, with the mixing parameter $x$ continuously varying over the entire composition range. We reveal that the mixed alloys ($x$ between 0.5 and 0.9) demonstrate smaller bandgaps than the pure Sb- and Bi-based compounds. The reduction in the bandgap of Cs$_2$AgBiBr$_6$ achieved through alloying (170 meV) is larger than if the mixed alloys had obeyed Vegard’s law (70 meV). Through in-depth computations, we propose that bandgap lowering arises from the type II band alignment between Cs$_2$AgBiBr$_6$ and Cs$_2$AgSbBr$_6$. The energy mismatch between the Bi and Sb s and p atomic orbitals, coupled with their non-linear mixing, results in the alloys adopting a smaller bandgap than the pure compounds. Our work demonstrates an approach to achieve bandgap reduction and highlights that bandgap bowing may be found in other double perovskite alloys by pairing together materials forming a type II band alignment.

Introduction

Despite the meteoric rise in efficiency of photovoltaics based on lead-halide perovskites,1,2 concerns remain over the toxicity of the lead component.3 Three of the main approaches to find lead-free alternatives are: (a) chemical substitution of Pb$_{2+}$ with more benign metal cations;4 (b) discovery of materials that could replicate the defect tolerance of the lead-halide perovskites;5,6 and (c) exploration of halide materials that maintain the perovskite crystal structure. The third route has led to extensive work on double perovskites, in which the toxic Pb$_{2+}$ cation is replaced with a pair of monovalent and trivalent cations (e.g., Ag$^+$ and Bi$_{3+}$).7–11 Double perovskites, or elpasolites, have the general formula A$_2$B$_x$iB$_{2-x}$mX$_6$, where A is a monovalent cation (such as Cs$^+$ or CH$_3$NH$_3$$^{+}$), B$_x$ a monovalent metal cation (such as Na$^+$, Cu$^+$, Ag$^+$ or Au$^+$), B$_{2-x}$m a trivalent metal cation (usually Sb$_{3+}$, Bi$_{5+}$ or In$_{3+}$) and X a halide anion (Cl$^-$, Br$^-$ or I$^-$).11–15 Calculations have shown that the bandgap can be tuned over a wide range by changing the species in each atomic site. There has been particular focus on Cs$_2$AgBiBr$_6$ for photovoltaic applications, and several groups have demonstrated long charge-carrier lifetimes, which can exceed a microsecond.13,16,17 Photovoltaic devices with Cs$_2$AgBiBr$_6$ have demonstrated high external quantum efficiencies reaching...
60%, with stable performance over hundreds of hours in ambient air. These promising charge transport properties, coupled with the improved stability of Cs$_2$AgBiBr$_6$ over lead-halide perovskites, have led to the material also being considered for photocatalytic applications.

However, the potential of Cs$_2$AgBiBr$_6$ for photovoltaic and photocatalytic applications is limited by the wide bandgap (2.1–2.3 eV) and its indirect nature, which limit light absorption. Efforts to achieve a smaller and more direct bandgap have involved alloying with TI, but this is more toxic than Pb. Alloying Cs$_2$AgBiBr$_6$ with the substantially less toxic Sb was also shown to be effective, but led to a smaller reduction in bandgap than TI alloying. In part, this was because the Sb-based double perovskite itself (Cs$_2$AgSbBr$_6$) has a wide bandgap of 1.9–2.1 eV. Another factor was that only a maximum of 37.5% Sb could be introduced through powder melt synthesis, limiting the extent of bandgap reduction. Intriguingly, mixed Cs$_2$Ag(Sb$_{1-x}$Bi$_x$)Br$_6$ alloys have exhibited a non-linear reduction in the bandgap, i.e., bandgap bowing, with increasing Sb content. Bandgap bowing has also been found in Pb/Sn perovskite alloys, and, in this case, the bowing is pronounced, such that the mixed alloy exhibits a smaller bandgap than either of the pure Pb- or Sn-based compounds.

So far, there is a lack of understanding of the extent of bandgap bowing in Sb–Bi double perovskite alloys and whether the mixed compositions could exhibit a smaller bandgap than the pure compounds. This requires the full composition range in Cs$_2$Ag(Sb$_{1-x}$Bi$_x$)Br$_6$ alloys to be synthesized. However, synthesizing phase-pure Cs$_2$AgSbBr$_6$ is challenging, particularly with increasing Sb content. Therefore, mixed Cs$_2$AgSbBr$_6$ and Cs$_2$AgBiBr$_6$ have the same cubic structure and space group ($Pm3m$). The lattice constants were found to be 11.184 Å for Cs$_2$AgSbBr$_6$ and 11.255 Å for Cs$_2$AgBiBr$_6$, with a continuous variation between these compositions.

### Results and discussion

**Synthesis and verification of composition**

Cs$_2$Ag(Sb$_{1-x}$Bi$_x$)Br$_6$ thin films were synthesized by solution processing. The CsBr, AgBr, SbBr$_3$ and BiBr$_3$ precursors were mixed according to their stoichiometric ratio in DMSO with a concentration of 0.5 mol L$^{-1}$. In contrast to the dipping method used by Liu et al.,$^{27}$ we used a lower annealing temperature and shorter annealing time (detailed in the Experimental section in the ESI†), which may have contributed to the successful synthesis of phase-pure Cs$_2$AgSbBr$_6$. Photographs of the films (approx. 200 nm thickness in all cases) are shown in Fig. 1a, and it was observed that the mixed compositions have a deeper color. To determine the bulk composition of the films, we performed RBS measurements (Fig. 1b and Table 1). It was found that the Sb/Bi ratio from the RBS measurements matched the stoichiometry in the precursor solution, deviating from the nominal precursor stoichiometry by up to 2.1 percentage points (Table 1). Since the Sb RBs peak is buried between two other peaks (Ag and Cs, see Fig. S1, ESI†), the fitting and statistical uncertainties are high when the Sb concentration is low. These deviations could arise from uncertainties in the RBS measurement, as well as errors in preparing the precursor solution. These measurements therefore indicate that there is no change in the bulk composition of the thin films during crystallization. However, the presence of phase-impurities in the films below the percent-level could not be excluded.

### Crystal structure and phase purity

The phase-purity of the films was determined through XRD measurements (Fig. 2a). Cs$_2$AgSbBr$_6$ and Cs$_2$AgBiBr$_6$ have the same cubic structure and space group ($Pm3m$). The lattice constants were found to be 11.184 Å for Cs$_2$AgSbBr$_6$ and 11.255 Å for Cs$_2$AgBiBr$_6$, with a continuous variation between these compositions.

![Fig. 1](image-url) (a) Photographs of the Cs$_2$Ag(Sb$_{1-x}$Bi$_x$)Br$_6$ films on glass under ambient lighting, with a thickness of approximately 200 nm. The Sb percentage labelled is that in the precursor solution. (b) Measurement of the bulk composition of Cs$_2$Ag(Sb$_{1-x}$Bi$_x$)Br$_6$ films with Rutherford Backscattering Spectrometry (fitting in Fig. S1, ESI†).
extremes through the alloying range, as could be seen from the continuous shift in peak positions (Fig. 2b and 3d). Common phase impurities for the Sb–Bi double perovskites are Cs3Bi2Br9 and Cs3Sb2Br9. Both impurities have almost the same diffraction patterns with their double perovskite counterparts, but one of the main differences is a peak from Cs3Bi2Br9 at 8.95 ˚C14o, or from Cs3Sb2Br9 at 9.10 ˚C14o. Neither impurity peaks were found to be present here. However, these XRD measurements were taken using a 1D linescan, and it is possible that the impurity peaks were not detected due to preferred orientation. We therefore performed 2D XRD measurements (Fig. S2, ESI‡). We synthesized the whole alloying range of double perovskite thin films and intentionally induced a Cs3(Bi,Sb)2Br9 phase impurity to the films with 50% Sb. From the 2D XRD patterns, we found that the diffraction peak should be detectable by the 1D linescan if it is present. Therefore, the absence of any phase-impurities in the 1D XRD patterns in Fig. 2a shows the films to be phase-pure. The diffraction patterns also showed no peak splitting, but the full width at half maximum (FWHM) of the pure Sb-based double perovskite and mixed alloys were larger than the Bi-based double perovskite (Fig. 2b and c). This could either be due to smaller grains or small amounts of phase segregation that could not be resolved. Scanning Electron Microscopy (SEM) measurements of the films showed that the Sb-based double perovskites and mixed alloys have smaller and less well-defined grains than the pure Bi-based double perovskite (Fig. S3, ESI‡), which is consistent with the larger FWHM in the diffraction patterns of Sb containing films. These XRD and SEM measurements, together with the RBS measurements matching the stoichiometry of the precursor solutions, are consistent with the alloys being homogeneous.

We note that previous works have reported that mixed Sb–Bi double perovskite alloys with high Sb contents have marginally lower stability. For example, Liu et al. found that Cs2Ag(Sb1−xBi1),Br6 thin films with x = 0.75 had AgBr and CsAgBr2. 

### Table 1

Quantification of the bulk composition of Cs2Ag(Sb1−xBi1),Br6 thin films by RBS

| Nominal Sb/(Sb + Bi) in precursor solution | Cs/at% | Ag/at% | Sb/at% | Bi/at% | Br/at% | Sb/(Sb + Bi) in film |
|-------------------------------------------|--------|--------|--------|--------|--------|---------------------|
| 100%                                      | 20.5   | 10.1   | 9.5    | 0      | 59.5   | 100%                |
| 90%                                       | 19.6   | 10.1   | 9.2    | 1.2    | 60.0   | 88.5%               |
| 70%                                       | 19.6   | 10.5   | 7.5    | 3.2    | 59.4   | 70.1%               |
| 50%                                       | 19.5   | 10.6   | 5.5    | 5.2    | 59.2   | 51.4%               |
| 20%                                       | 19.8   | 10.4   | 2.3    | 8.1    | 59.4   | 22.1%               |
| 0%                                        | 19.8   | 10.0   | 0      | 10.1   | 60.1   | 0%                  |

Fig. 2  (a) XRD pattern of the Cs2Ag(Sb1−xBi1),Br6 films over the composition series. The reference patterns of Cs2AgSbBr6 and Cs2AgBiBr6 calculated from their crystallographic information files are denoted as Sb Ref and Bi Ref respectively.12,15 (b) Full width half maximum (FWHM) of the (022) peak for different compositions. (c) FWHM of different diffraction peaks and the average grain size calculated using the Scherrer equation for different compositions.
decomposition products after 4 h annealing at 250 °C.⁷ However, the diffraction peaks of these phases were small compared to the main double perovskite peaks, showing the degree of degradation to be small.⁷ Sb–Bi double perovskites with lower Sb contents have been found to have comparable thermal and environmental stability as Cs₂AgBiBr₆.⁶,⁷ Furthermore, the reported stability of mixed Sb–Bi double perovskites is significantly improved over MAPbI₃ thin films, which degrades in ambient air within 5 days⁸ and decomposes to form a significant fraction of PbI₂ after 35 min at 150 °C.⁹

Absorption, bandgap and band positions

Standard optical transmittance and reflectance measurements (using a UV-visible spectrophotometer with an integrating sphere) were used to determine the absorption coefficient of the double perovskite thin films (Fig. 3a). All films showed a slow increase in the absorption coefficient for photon energies > 2 eV, before rising sharply to >10⁵ cm⁻¹ at >2.6 eV. An absorption coefficient exceeding 10⁵ cm⁻¹ at >2.6 eV is characteristic of a direct band-to-band transition. Both Cs₂AgBiBr₆ and CsₓSbₓAgBiBr₆ have indirect bandgaps due to the effects of the Ag d orbitals at the band-edges, and the alloys are also expected to have indirect bandgaps.⁴ Therefore, to determine the indirect bandgap, we investigated the absorption onset in the lower photon energy range (i.e., between 2–2.6 eV), leaving the discussion of the absorption in the higher photon energy range to later in the paper. We observed that the alloys with 70–90% Sb showed a lower-energy absorption onset than the pure Sb- and Bi-based films. However, the indirect bandgaps resulted in the absorption coefficients being small close to the band-edge, making it difficult to accurately determine the bandgap from standard transmittance and reflectance measurements. Therefore, we performed PDS measurements, which are sensitive to the absorbance 3–4 orders below the band-edge (operating details in the Experimental section, ESI †).

A consequence of the high sensitivity to low absorbance is that the measurements in PDS saturate for high absorbance at >2.6 eV (Fig. 3b), and the peaks in the absorption coefficient seen in Fig. 3a are not observed in the PDS measurements plotted on a semi-logarithmic scale (see later in the paper for a discussion of these peaks). The normalized absorbance from PDS measurements at the band edge (in the range of 2–2.3 eV) is approximately 3 orders of magnitude lower than the absorbance at 2.6 eV, where the absorption coefficient is >10⁵ cm⁻¹ (Fig. 3a). Thus, the absorption coefficient at the band edge should be on the order of 10⁵ cm⁻¹. We note that silicon, which is a typical indirect bandgap material, has an absorption coefficient of 10⁵ cm⁻¹ at the band edge.⁵,⁶

The absorption plots shown in Fig. 3b do qualitatively indicate an exponentially increasing absorption coefficient versus energy, which appears linear on a semi-logarithmic plot. The double perovskites with x ranging from 0 to 0.7 have similar slopes in their absorption onsets when plotted on a semi-logarithmic scale. For x = 0.9 and the pure Sb-based compound, the slopes are shallower. Increasing the fraction of Sb (x) from 0 (pure Bi) to 0.5 reveals a red-shift in the absorption onset. The double perovskites with x = 0.7 and x = 0.9 all have similar absorption onsets to the material with x = 0.5. These mixed alloys with x = 0.5–0.9 all have absorption onsets that are red-shifted to the pure Sb-based compound, as well as the pure Bi-based compound. Therefore, alloys with 50–90% Sb demonstrate smaller bandgaps than either of the pure end double perovskites. To extract numerical values of the bandgap and quantify their variation with composition, we fitted the PDS absorbance data using a Tauc plot, which is a plot of (αhv)¹/² against hv. The rationale can be seen from eqn (1).
(ahr)^1/n = A(hv - E_g) \tag{1}

where \( \alpha \) is the absorption coefficient, \( h \) is Planck’s constant, \( \nu \) is the photon frequency, \( A \) is a proportionality constant, \( E_g \) is the bandgap, and \( n = 2 \) for an indirect bandgap.\textsuperscript{35,36} Therefore, by plotting \((ahr)^{0.5}\) against \((h\nu)\), the bandgap can be extracted from the intercept between the tangents fit to the absorption onset and background (Fig. 3c). From these Tauc plots, we found the system to exhibit significant bandgap bowing (Fig. 3d). The compound with \( x = 0.9 \) demonstrated the lowest bandgap of 2.08 eV, which is smaller than the bandgap of Cs\(_2\)AgSbBr\(_6\) (2.28 eV) and Cs\(_2\)AgBiBr\(_6\) (2.25 eV). We note that the bandgaps extracted from a Tauc plot can be affected by the absorbance at the band-edge and the steepness of the absorption onset. Cs\(_2\)AgBiBr\(_6\) (and Cs\(_2\)AgSbBr\(_6\)) thin films have very low absorbance at the band-edge due to the indirect bandgap and the low quantity of material. Therefore, their bandgaps extracted from Tauc plots have tended to be higher than the bandgaps extracted in single crystals or powders, which have bandgaps extracted from Tauc plots have tended to be higher than the bandgaps extracted from Tauc plots have tended to be higher than the bandgaps extracted from Tauc plots have tended to be higher than the bandgaps extracted from Tauc plots have tended to be higher than the bandgaps extracted from single crystals or powders, which have.

Electronic structure and bandgap lowering mechanism

To understand the atomistic origin of the bandgap lowering in the Sb–Bi double perovskites, calculations of the electronic structure were performed. The band structure and density of states for pure Sb and Bi double perovskites are shown in Fig. 4a–d. In agreement with previous literature, as well as our optical measurements in Fig. 3, both Cs\(_2\)AgSbBr\(_6\) and Cs\(_2\)AgBiBr\(_6\) were found to have an indirect bandgap,\textsuperscript{25,27,29} with the valence band maximum (VBM) located at the X point and the conduction band minimum (CBM) at the L point in reciprocal space. Using relativistic hybrid density functional theory (HSE06 including spin–orbit coupling), the indirect bandgap and first direct transition of Cs\(_2\)AgSbBr\(_6\) were calculated to be 1.37 and 2.60 eV, respectively. Analysis of the electron band orbital character revealed the conduction band states to be dominated by anti-bonding Sb 5p–Br 4p interactions, while the valence band states primarily arise from Sb 5s, Ag 4d and Br 4p orbital interactions. The Cs\(_2\) cations act as spectator ions, as noted in the literature,\textsuperscript{29} with a relatively large nearest-neighbor distance to Br\(^-\).

Likewise, the indirect bandgap and direct transition of Cs\(_2\)AgBiBr\(_6\) were calculated to be 1.77 and 2.49 eV, respectively. Due to the stronger spin–orbit coupling of the Bi 6p orbitals, the direct bandgap of Cs\(_2\)AgBiBr\(_6\) is slightly reduced from that of Cs\(_2\)AgSbBr\(_6\), despite a larger fundamental gap, and is located at a different point in reciprocal space (X = (0.5, 0.5, 0.5), cf. b = (0.5, 0.38, 0.62) for Cs\(_2\)AgSbBr\(_6\)). Similarly, the conduction band states are dominated by anti-bonding interactions between the trivalent pnictogen cation (Bi 6p) and the halide anion (Br 4p) orbitals, while the valence band states primarily arise from Bi 6s, Ag 4d and Br 4p orbital interactions. Notably, the larger band gap of Cs\(_2\)AgBiBr\(_6\) relative to Cs\(_2\)AgSbBr\(_6\) is an interesting exception to the typical trend of decreasing bandgap upon atomic substitution with heavier members from the same periodic group, which has been observed for other perovskite materials.\textsuperscript{13,40,41}

To delve closer to the origin of bandgap lowering, the ‘natural’ band offset of the two double perovskite materials was calculated following the alignment procedure of Butler et al.,\textsuperscript{42} with the resulting electron band alignment diagram shown in Fig. 4e. Our investigations indicate a type II ‘staggered gap’ alignment, with a valence band offset (VBO) of 0.75 eV and a conduction band offset (CBO) of 0.34 eV (Cs\(_2\)AgSbBr\(_6\) above Cs\(_2\)AgBiBr\(_6\) in both cases). Typically, the energies of valence electrons become less negative as one moves down a group in the periodic table, corresponding to a decrease in ionization energies. However, for Bi\(^{3+}\) and Sb\(^{3+}\), this is not the case, with the Bi\(^{3+}\) 6s\(^2\) lone pair being lower in energy than the Sb\(^{3+}\) 5s\(^2\) lone pair.\textsuperscript{43} This is a result of the relativistic contraction of the Bi 6s orbital, due to its large atomic number, resulting in a more localized, lower-energy valence s orbital, compared to Sb 5s.\textsuperscript{44}

Consequently, the more-diffuse, higher-energy Sb 5s\(^2\) lone pair has a stronger interaction with the Ag 4d and Br 4p
orbitals, due to a reduced energy separation of the bonding orbitals (Fig. S12, ESI†). This produces both greater dispersion in the valence band and a higher VBM, as shown in Fig. 4e. In a similar manner, the elevated position of the CBM in Cs2AgSbBr6 can be understood by considering the ionization energies and ionic orbital energies. While the first ionization energy of Sb is indeed larger than that of Bi, the third ionization energy (corresponding to the removal of a p electron from Sb3+/Bi3+) is in fact 0.3 eV lower for Sb than for Bi,43 indicating higher energy cationic p states. When the pnictogen elements are in the +3 oxidation state, as is the case in these materials, the third ionization energy provides an improved estimate for the energy of the unoccupied p orbitals. Hence, we argue that, in the +3 formal charge state, the Sb valence p orbitals are in fact higher in energy than those of Bi, suggesting a higher energy CBM for Cs2AgSbBr6, as witnessed in our investigations.

The origins of bandgap bowing in semiconductor alloys are typically due to chemical effects (e.g., differences in electronegativity), local size-mismatch effects or changes in the lattice parameter.45–47 For the Pb–Sn perovskite alloy system, Im et al. attributed bandgap bowing to the combined effect of spin–orbit coupling and composition-induced phase change.48 Snith and coworkers proposed that the short range ordering of preferred atomic scale clusters allow the bandgap of the mixed alloy to be lower than that of both pure compounds.29 In contrast, Stevanović and coworkers found that the strong nonlinearity in bandgap was primarily due to the mismatch in energy between s and p atomic orbitals of Pb and Sn.28 The Pb–Sn alloys have a higher VBM dominated by Sn-5s and I-5p orbitals and lower CBM dominated by Pb-6p and I-5p orbitals. They found that spin–orbit coupling, structure changes and short-range ordering did not have a significant effect on bandgap bowing, and proposed that a homogeneous structure would have improved stability over a structure with short range ordering.

In the case of Cs2Ag(Sb,Bi1−x)Br6, we propose that the type II staggered gap alignment between the pure compounds allows for the non-linear mixing of electronic states such that bandgaps lower than that of either pure material are obtained (Fig. 4e). Upon addition of Bi to the pure Sb double perovskite, the conduction band will be lowered because the CBM wavefunction amplitude is preferentially allocated to the Bi sites, producing a ‘Bi-like’, lower-energy conduction band state. The presence of Bi will also enhance spin–orbit coupling, further reducing the energy of the CBM. On the other hand, the highest energy valence band state will remain ‘Sb-like’, with greater wavefunction amplitude at the Sb sites yielding a VBM only slightly below that of the pure Sb material. This mixing of electronic states in the alloys to produce a low-energy CBM, dominated by Bi–Br interactions, and a high-energy VBM, dominated by Sb–Ag–Br interactions, produces bandgaps in the double perovskite alloys which are lower than that of either pure material. Indeed, this prediction is supported by electronic structure calculations for the alloys (assuming a uniform atomic distribution), which show reduced bandgaps due to the expected orbital mixing at the band edges (Fig. S13–S15 and Table S3, ESI†). These predictions are further supported by the experimentally-determined band positions of the Cs2Ag(Sb,Bi1−x)Br6 compounds (Fig. 3e), which show the electron affinities of the mixed alloys to be close to Cs2AgBiBr6. The ionization potentials of the mixed alloys with x = 0.5–0.9 are in between those of the pure compounds. This accounts for the reduction in their bandgap compared to Cs2AgBiBr6. The reduction in the bandgaps of the x = 0.5–0.9 mixed alloys compared to Cs2AgSbBr6 are due to the increase in ionization potential being...
smaller than the increase in electron affinity when Bi is added to Cs$_2$AgSbBr$_6$, as discussed earlier.

Notably, this combination of a low-energy CBM with a high-energy VBM is expected to allow for enhanced doping and hence increased carrier concentrations in the alloy, relative to the pure materials.\cite{21, 22, 23} In particular, the raised VBM, relative to pure Cs$_2$AgBiBr$_6$ (which has been reported as intrinsically p-type),\cite{24, 25, 26} should allow for greater hole carrier concentrations in the reduced-bandgap alloy. This is supported by our X-ray photoemission spectroscopy measurements, which show a reduction in the valence band to Fermi level offset when Sb is alloyed into Cs$_2$AgBiBr$_6$, showing the materials to become more p-type (Table S1, ESI).\cite{21, 22, 23}

As the alloy mixing parameter $x$ approaches extreme values ($x \rightarrow 0$ or $x \rightarrow 1$), the ability of the band extrema states to simultaneously adopt Bi and Sb character is diminished, hence the bandgap increases toward the pure double perovskite values. Therefore, we propose that this orbital-mixing behavior, facilitated by the type II bandgap alignment, is the origin of the non-linear, non-monotonic variation in bandgap with composition in the Sb–Bi double perovskite system.

Another possible contribution to bandgap bowing is volume deformation, whereby variation in the lattice constant upon alloying results in non-linear transformation of the electronic structure.\cite{27} This mechanism, however, more commonly dominates in alloys involving more chemically-distinct materials than is the case here. Moreover, due to the small positive bandgap deformation potentials calculated for the Sb and Bi compounds ($\Delta E_g \sim 0.02$ eV), we rule out this mechanism. Relative to the experimentally-observed bowing ($\sim$0.1 eV, Fig. 3d), volume distortion alone is not the origin of bandgap bowing in this alloy system.

Finally, we return to discuss the sharp peak in the absorption coefficient of the films at $>2.6$ eV (Fig. 3a). This is especially evident for Cs$_2$AgBiBr$_6$. Previous work attributed the sharp absorption peak in Cs$_2$AgBiBr$_6$ to an exciton associated with the direct transition.\cite{28, 29, 30} However, there is also the possibility that these features in the pure compounds and mixed alloys are due to a narrow density of states at the band-edges. To explore this possibility, we computed the absorption spectra for Cs$_2$AgSbBr$_6$ and Cs$_2$AgBiBr$_6$ without excitonic effects (Fig. 4f). These spectra were broadened by convoluting with a Gaussian peak with a FWHM of 0.15 eV. For both materials, the calculated absorption spectra exhibit peaks at 2.8 eV, in agreement with the experimental measurements. These peaks arise from the relatively-weak dispersion of the electron bands at the CBM and VBM of the materials (Fig. 4a and b), yielding peaks in both the density of states (Fig. 4c and d) and thus the optical absorption (Fig. 4f). This strongly suggests that the peaks observed in the experimental UV-visible measurements are the result of direct transitions between the relatively-flat electron bands. That said, the exciton binding energy of Cs$_2$AgBiBr$_6$ was calculated to be 167 meV within effective mass theory, which is sufficiently large that stable exciton formation is possible in these systems.

Curiously, the computed absorption spectrum for Cs$_2$AgSbBr$_6$ shows a distinct absorption peak (Fig. 4f), whereas the measured peak from UV-visible spectrophotometry became less distinct with increasing Sb content, until there was barely an observable peak for the pure Sb-based compound (Fig. 3a). This may have been due to a ‘smearing out’ of the absorption peak due to structural disorder.\cite{31, 32, 33} We calculated the absorption spectra for the pure Sb-based compound convoluted with Gaussian peaks with wider FWHM (0.2 eV, 0.3 eV, 0.4 eV; Fig. S16, ESI).\cite{31, 32, 33} These show that the peak becomes indistinguishable when broadening is large, as witnessed experimentally and consistent with the PDS measurements. Thus, peak broadening as a result of disorder leads to the observed ‘smear-ed-out’ absorption spectrum in Fig. 3a.

**Conclusions**

In conclusion, we successfully synthesized phase-pure Cs$_2$AgSbBr$_6$ thin films, as well as Cs$_2$Ag(Sb$_x$Bi$_{1-x}$)Br$_6$ with $x$ varying over the full composition range. In doing so, we found that the mixed double perovskites with $x$ between 0.5 and 0.9 to have the smallest bandgaps, lower than those of the pure compounds. From the electronic band alignment, we found that the origin of bandgap bowing in this double perovskite alloy is due to chemical rather than structural effects. The type II band alignment between Cs$_2$AgBiBr$_6$ and Cs$_2$AgSbBr$_6$, in combination with non-linear mixing of the electronic states, results in the alloy having smaller bandgaps than either pure material. Our work demonstrates a novel route to reduce the bandgap of Cs$_2$AgBiBr$_6$ and Cs$_2$AgSbBr$_6$, which could be generalized to other halide double perovskites. That is, we propose that alloys formed from compounds with a type II band alignment could exhibit similar bandgap lowering. This may prove crucial for improving the suitability of double perovskites for photovoltaic and photocatalytic applications.

**Author contributions**

Z. L. synthesized the Sb–Bi double perovskite thin films, took photographs, and performed 1D XRD, SEM and UV-visible spectrophotometry measurements. S. R. K. performed the theoretical calculations and analyzed the results, along with D. W. D., D. O. S. and A. W. M. N. analyzed the RBS results, which were collected by M. L. and J. J. R. G. P. measured the 2D XRD data. M. A.-J. and Z. A.-G. measured and analyzed the PDS data. M. I. performed the PES measurements. R. H. F. supervised Z. L. and contributed to the discussion. R. L. Z. H. conceived of the project and supervised the work. All authors discussed the results and contributed to writing the paper.

**Conflicts of interest**

There are no conflicts of interest to declare.

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