Accepted Article

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To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201807421
Angew. Chem. 10.1002/ange.201807421

Link to VoR: http://dx.doi.org/10.1002/anie.201807421
http://dx.doi.org/10.1002/ange.201807421
Small-Bandgap Halide Double Perovskites

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Abstract: Despite their compositional versatility, most halide double perovskites feature large bandgaps. Herein, we describe a strategy for achieving small bandgaps in this family of materials. The new double perovskites Cs₂AgTlX₆ (X = Cl (1) and Br (2)) have direct bandgaps of 2.0 and 0.95 eV, respectively, which are ca. 1 eV lower than those of analogous perovskites. To our knowledge, 2 displays the lowest bandgap for any known halide perovskite. Unlike in A/BB′X₆ perovskites, the bandgap transition in A₂BB′X₆ double perovskites can show substantial metal-to-metal charge-transfer character. We demonstrate how this band-edge orbital composition can be used to achieve small bandgaps through the selection of energetically aligned B- and B′-site metal frontier orbitals. Calculations reveal a shallow, symmetry-forbidden region at the band edges for 1, which results in long (∼µm) microwave conductivity lifetimes. We further describe a facile self-doping reaction in 2 through Br₂ loss at ambient conditions.

The exceptional optoelectronic properties of lead-halide perovskite solar-cell absorbers have instigated a renewed interest in this well-known family of materials. Although optimization of these absorbers has afforded record solar-cell efficiencies,[b] there is now growing appreciation for the potential of new perovskite compositions.[c] Studying analogs is a time-tested method for understanding the origins of a champion material’s remarkable properties and establishing design rules for realizing these properties in alternative compositions.[d] To access greater compositional variation within the perovskite lattice, we and others[e] recently explored the photophysical properties of the A₂BB′X₆ (X = halide) double perovskite platform. Unlike A/BB′X₆ perovskites, which are restricted to 2+ B-site cations, double perovskites can support oxidation states from 1+ to 4+ for the B- and B′-site metals. This compositional flexibility should afford diverse electronic structures, as observed in oxide perovskites, which range from insulators to metals.[f] However, to date, the vast majority of halide double perovskites are either chlorides or bromides with bandgaps >ca. 2 eV. Indeed, halide substitution has been the most explored method for reducing the bandgap in halide perovskites, with iodides affording the lowest bandgaps.[g] Herein, we demonstrate that double perovskites enable a different method for creating small bandgaps—through the energetic alignment of the frontier orbitals of the B and B′-site metals. This strategy allows us to form chloride and bromide double perovskites with bandgaps that are ca. 1 eV smaller than those of analogous perovskites with the same halide. To our knowledge, the bromide perovskite features the smallest bandgap reported for a halide perovskite since their discovery in 1883.[h]

Crystalline powders of Cs₂AgTlCl₆ (1) and Cs₂AgTlBr₆ (2) were precipitated from solutions containing Tl₂O₃, CsX, and AgX (X = Cl, Br) in 6M HCl and 9M HBr, respectively. Importantly, the stoichiometric precursors produce mixtures of Cs₃Tl₂X₉ and AgX, and the double-perovskite phase forms only upon addition of several equivalents of CsCl (for 1) or AgBr (for 2) (see Supporting Information (SI)). Slowly cooling the solutions from 100 °C to room temperature produces crystals suitable for single-crystal X-ray diffraction (XRD) (Table S1), which reveals a cubic double perovskite structure (Figures 1, S1) with Fm-3m symmetry, consisting of a 3D network of corner-sharing halide octahedra with alternating Ag₃ and Tl₃ centers. For both 1 and 2, the Ag–X bond distances are unchanged from the related Cs₂AgBiX₆ structures,[i] while the Tl–X bonds are ca. 0.1 Å shorter than the Bi–X bonds (Table S2). Recently, we demonstrated that dilute alloying of Tl³⁺ (<1 atom%) into Cs₂AgBiX₆ afforded a large bandgap reduction, from 1.95 to ca. 1.5 eV in Cs₂Ag(Bi₁₋ₓTlₓ)Br₆ (x = 0.075).[j] This alloyed material is effectively a Tl³⁺/Bi³⁺ solid solution where now both x = 0 and x = 1 endpoints are known (Figure 1).

The optical absorption properties of 1 and 2 (Figure 2A) were determined by diffuse reflectance measurements on polycrystalline powders. Reflectance spectra are particularly sensitive to particle size,[k] so we performed our optical analyses on dispersions of small (≤ 1 μm) particles to eliminate effects of weakly absorbing defects (see Figure S2 and the SI).[l] Submicron-sized particles were formed through rapid precipitation of a hot precursor solution in liquid N₂ (see SI). The reflectance spectra were converted to pseudo-absorption spectra using the Kubelka-Munk transformation.[m] Tauc plots of the transformed data, assuming a direct, forbidden transition (discussed later), place the bandgap of 1 at 1.96 eV and of 2 at 0.95 eV (Figure S3). Bandgap estimates vary based on measurement and data fitting methods and we report the highest measured values (see discussion in the SI). These values are strongly red-shifted from typical values for chloride (2.5 – 3.3 eV)[n] and bromide (1.8 – 2.3 eV)[o] perovskites. Notably, the bandgap of the bromide perovskite 2 is significantly smaller than those observed for iodide perovskites (1.2 – 1.6 eV).[p,q] As described later, a symmetry-forbidden band-edge transition in 1 and 2 could cause overestimation of the bandgap by ca. 0.2 eV. Thus, to the best of our knowledge, 2 possesses the smallest reported bandgap for a halide perovskite.
COMMUNICATION

We observe no photoluminescence (PL) in 1 and 2 (even at 20 K) despite their calculated direct bandgaps (see below), which typically lead to rapid radiative carrier recombination. A similar lack of band-edge PL in the direct bandgap, isoelectronic double perovskite Cs₂AgInCl₆ has been attributed to a symmetry-forbidden bandgap transition.¹⁶ We calculated the transition dipole matrix elements along the high-symmetry lines L → Γ and Γ → X of 1 using (generalized) Kohn-Sham eigenstates from density functional theory (DFT) in the independent particle approximation with the experimental crystal structure (Figure 2B; see SI for details). Indeed, our DFT calculations show that at Γ and along Γ → X the dipole matrix elements are identically zero, representing a series of symmetry-forbidden transitions (see SI). The frequency-dependent linear absorption spectrum, calculated using the ab initio GW-Bethe-Salpeter approach (see SI) exceeds 10⁴ cm⁻¹ only 0.17 eV above the band edge (Figure 2C), indicating that the region in k-space associated with symmetry-forbidden transitions in these materials is small (smaller than the 0.27 eV region in Cs₂AgInCl₆; See SI Figure S13). Thus, although symmetry-forbidden transitions are present in 1 and 2, they appear to have a relatively minor effect on the absorption properties. After excitation, carriers thermalize into the forbidden region and largely remain there as the energy width of the forbidden region (170 meV) is several times that of thermal energy at room temperature (26 meV). Carriers confined to the forbidden region cannot recombine radiatively, explaining the materials’ lack of PL. Notably, this results in µs-long carrier recombination lifetimes in 1, observed through time-resolved microwave conductivity measurements (Figures 2D, S8-9), which are more typically seen in indirect-gap semiconductors. A similar case has been observed, and intensely studied, for the high-performing perovskite solar-cell absorber (CH₃NH₃)PbI₃.¹⁹

To understand the origin of the small bandgaps in 1 and 2, we performed calculations with ab initio many-body perturbation theory in a “one-shot” G₀W₀ approach, including spin-orbit corrections (SOCs).²⁰ G₀W₀ calculations reliant on DFT starting points with (semi)local exchange-correlation functionals greatly underestimate experimental bandgaps of Tl- and Pb-containing perovskites.²¹ We therefore used the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06) as a starting point for our G₀W₀ calculations, as implemented in VASP. I.e., we use DFT-HSE to construct the zeroth-order Green’s function G₀ and screened Coulomb interaction W₀ (see SI). Our calculated G₀W₀@HSE06 bandgap for 1 is 1.9 eV, in very good agreement with the experimental bandgap of 1.96 eV. For 2 the G₀W₀@HSE06 bandgap underestimates the experimental gap of 0.95 eV by more than 0.3 eV. Self-consistency in the eigenvalues (GW₀) can afford better agreement with experiment:²¹ the G₀W₀@HSE06 bandgap for 2 is 0.8 eV (Table S3). The DFT-HSE-

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**Figure 1.** Single-crystal structures of A) Cs₂AgBiBr₆ and C) Cs₂AgTlBr₄ (2). The structure in (B) of Cs₂Ag(Bi₁₋ₓTlx)Br₆ is for illustration only. Black, orange, white, brown and turquoise spheres represent Tl, Bi, Ag, Br, and Cs atoms, respectively. Photographs of Cs₂AgBiBr₆ (left) and 2 (right) crystals. Photograph and structure of Cs₂AgBiBr₆ (Figure 1A) adapted with permission from J. Am. Chem. Soc. 2016, 138, 2138-2141. Copyright 2016 American Chemical Society.

**Figure 2.** A) Absorption spectra of 1 and 2 (solid lines) compared to those of Cs₂AgInCl₆ and Cs₂AgBiBr₆ (dashed lines). B) Transition dipole matrix elements (|P|²) along high-symmetry lines in reciprocal space calculated within the independent particle approximation. C) Absorption spectrum of 1 calculated using the ab initio GW-Bethe-Salpeter approach. The red box highlights the symmetry-forbidden region. D) Time-resolved microwave conductivity traces of crystals of 1 showing µs-long conductivity. Samples were excited at 2.06 eV.
We attribute the small observed bandgaps in 1 and 2 to a combination of two factors. First, the presence of diffuse, spherical Tl$^+$ 6s (and some Ag$^+$ 5s) orbitals at the conduction band minimum (CBM) leads to large overlap with the halide orbitals and consequently a highly dispersive conduction band. This is evidenced by the small electron effective mass calculated for 1 ($m^*_e = 0.23$, Table S4). Highly dispersive bands are correlated with small bandgaps as increasing bandwidth brings band extrema closer together. Second, a low bandgap is consistent with a small intrinsinc energy difference between filled Ag 4d and vacant Tl 6s orbitals, inherited from the atomic limit (Figure 3C). In 1 and 2 the CBM contains mostly Tl-centered orbitals (with minor contributions from empty Ag 6s orbitals) while the valence band maximum (VBM) is dominated by Ag-centered orbitals. Consequently, the bandgap transition may be considered predominantly a metal-to-metal charge transfer (MMCT). Many double perovskites have similar MMCT character in their band edges and thus their bandgaps depend strongly on the energy spacing between the two metals' frontier orbitals. For example, Cs$_2$AgBiCl$_6$ and Cs$_2$AgTiCl$_6$ are isostructural with 1 and represent a single substitution at the B site, replacing either Bi$^+$ or Tl$^+$ with Ag$^+$ or Tl$^+$, respectively. However, with bandgaps of 2.77 eV and ~2.5 eV for Cs$_2$AgBiCl$_6$ and Cs$_2$AgTiCl$_6$, respectively, these materials are more typical chloride perovskites. The >0.5 eV energy difference between the bandgaps of these compounds and that of 1 demonstrates that it is only in combination that Ag$^+$ and Tl$^+$ yield reduced bandgaps. To further validate this claim, we used the WANNIER90 code to construct a tight-binding Hamiltonian of 1 and Cs$_2$AgBiCl$_6$ in a basis of maximally localized Wannier functions centered at each atomic site (Figure S12). We find that the energy difference between the on-site energies (Table S5) of filled Ag 4d and vacant Tl 6s orbitals (in the VBM and CBM of 1, respectively) is only 2.3 eV whereas that between filled Ag 4d and vacant Bi 6p orbitals (in the VBM and CBM of Cs$_2$AgBiCl$_6$, respectively) is 4.8 eV. This analysis confirms that the frontier molecular orbitals derived from Ag$^+$ (4d$^{10}$) and Tl$^+$ (6s$^2$) atomic orbitals (and halide orbitals) lie relatively close in energy, and bands with these orbital characters also lie closer together compared to double perovskites with a greater energetic mismatch between the frontier orbitals of the two B-site metals (Figure 3C).

Substitution of Tl$^+$ for Bi$^+$ in Cs$_2$AgBiBr$_6$ also results in a shift of the CBM from L to Γ and of the VBM from X to Γ yielding a direct bandgap in 2. As we previously reported, substitution of Tl$^+$ for Bi$^+$ in the solid solution Cs$_2$Ag(Bi$_{1-x}$Tl$_x$)Br$_6$ (x ~ 0.06) generates a new impurity band derived mostly from Tl 6s orbitals, which lies below the host lattice's CBM. Consistent with those results, the conduction band in 2 has predominantly Tl 6s character (Figure S10). In 2, the CBM occurs at the Γ point due to the pure s character of that band; in contrast, Cs$_2$AgBiBr$_6$ has mixed s and p character in its conduction band. The Cs$_2$AgBiCl$_6$ valence band (Figure 3A) features both Bi 6s and Ag 4d character. The Cs$_2$AgBiBr$_6$ valence band is similar. When Bi$^+$ is replaced with Tl$^+$, the loss of Bi 6s character decreases the energy of the band at the X point. In contrast, the energy of the Γ point is unaffected, and it becomes the new VBM in 2, yielding a direct gap.

We obtained alternating-current conductivity measurements on single crystals of 2 with graphite contacts using the Van der Pauw method (Figure 4 inset, Figures S4-S5). The graphite contacts act as ion-blocking electrodes and isolate the material's electronic response. Most metals react with halide perovskites and are unsuitable as electrodes. The electronic conductivity of 2 increases rapidly with time upon removing the crystal from the supernatant (Figure S6). Crystals grown from HBr solutions containing 200 mM dissolved Br$_2$ have ca. one order of magnitude higher initial conductivity than those grown without Br$_2$. Additionally, the headspace gas above crystals of 2 contains molecular Br$_2$, which brominates alkenes and can be observed by mass spectrometry (Scheme S1, Figure S7). Most strikingly, when crystals that have been separated from the mother liquor for several days are soaked in a gaseous Br$_2$ atmosphere (0.22 atm), using the apparatus shown in Figure 4, the crystals' conductivity decreases from $10^{-3}$ S/cm to $10^{-8}$ S/cm and increases again upon...
Where loss of neutral Br (as Br2 from the surface) is coupled to the moist air form a transparent insulating surface layer after ca. 24 h. Simultaneous formation of cationic halide vacancies (V_Br^2) in Cs2AgITlIIICl6 (2) represent a Br atom at a Br site in the lattice). Changes in the conductivity of a single crystal of 2 exposed to moist air form a transparent insulating surface layer after ca. 24 h.

Together these results point to a spontaneous defect reaction where loss of neutral Br (as Br2 from the surface) is coupled to the simultaneous formation of cationic halide vacancies (V_Br^2) and n-type doping of the material (through the addition of electrons, e^-):

\[ 2 \text{Br}_2 \rightarrow \text{Br}_2(g) + 2V_{\text{Br}} + 2e^- \]

(Br2Br represents a Br atom at a Br site in the lattice). Changes in self-doping appear to be diffusion-limited, and thus this reaction is likely facile and reversible. Therefore, the crystal spontaneously loses Br2 and self-dopes as it equilibrates with the atmosphere devoid of Br2. This process is analogous to the well-studied oxygen-exchange reaction observed in many oxides, including oxide perovskites.24 Equilibration of defect concentrations with I2 pressure at 120 °C has been observed in (CH3NH3)PbI3 pellets.25 Highly oxidized perovskites, such as Cs2SnIVI617c,26 and Cs2PdIVBr6,27 also display a propensity for n-type doping, with calculations suggesting halide vacancies as compensating defects. Due to limited crystal size we could not obtain similar measurements on 1. However, we expect halogen loss to occur at higher temperatures in 1 due to the more positive reduction potential of chlorine and the increased strength of metal-chloride bonds.

Even under high Br2 pressures (0.22 atm), 2 appears to remain n-type. The conductivity increases monotonically with Br2 loss rather than displaying a minimum (corresponding to a transition from p-type to intrinsic to n-type). This suggests that achieving p-type doping in 2 will be difficult except under highly oxidizing conditions. This spontaneous self-doping will lead to a substantial vacancy and electron concentration in 2 over time unless properly encapsulated. This defect population could also contribute to the lack of PL in these materials.

The new double perovskites Cs2AgITlIIICl6 (1) and Cs2AgTIIVIBr6 (2) display direct bandgaps that are ca. 1 eV smaller than those of analogous perovskites. To our knowledge, 2 has the lowest bandgap of any halide perovskite at 0.95 eV. We also describe a halogen degassing and self-doping reaction in 2 that is likely general to halide perovskites and analogous to the well-known role of oxygen partial pressure in oxide electrical transport properties. Thus far, mostly iodide perovskites have displayed suitable bandgaps (Eg ~ 1.4 eV)28 for absorbers in single-junction solar cells. Smaller-bandgap perovskites (Eg ~ 1.0 eV)29 are sought for perovskite-on-perovskite tandem solar cells. Importantly, 1 and 2 demonstrate that bromides and chlorides do not limit us to large bandgaps. The toxicity of TI should be considered with respect to any applications of 1 and 2. However, the fundamental design rules stated here are applicable to a very large family of materials and 1 and 2 are ideal model systems for demonstrating the electronic effects of B-site substitution. The group-14 ABX3 perovskites have ns2 and np2 orbitals of the same metal in their VBM and CBM, respectively. In contrast, the bandgap transition in double perovskites features a charge transfer between two different metals, allowing wide control of the bandgap through appropriate choice of B-site-metal pairs. All halide perovskites have bandgaps >1.2 eV, although material compression has led to bandgap closure.30 The strategy described here for accessing small bandgaps should be important for further expanding the electronic portfolio of this important family of materials, whose full technological utility is still being revealed.

![Figure 4](image-url) Apparatus used to expose crystals of 2 to a known pressure of Br2. The system is maintained under static vacuum and a partial pressure of 0.22 atm Br2 is obtained with a 19 °C water bath. Inset: Photograph of a single crystal of 2 with carbon contacts in a 4-point probe configuration.

![Figure 5](image-url) Changes in the conductivity of a single crystal of 2 over time due to the loss and reabsorption of Br2. Time zero corresponds to removal of the crystal from the Br2 atmosphere.

Figure 4. Apparatus used to expose crystals of 2 to a known pressure of Br2. The system is maintained under static vacuum and a partial pressure of 0.22 atm Br2 is obtained with a 19 °C water bath. Inset: Photograph of a single crystal of 2 with carbon contacts in a 4-point probe configuration.
Acknowledgements

We thank S. Weber for valuable discussions and K. Walker for experimental assistance. This work was funded by the Department of Energy, Laboratory Directed Research and Development program at SLAC National Accelerator Laboratory (DE-AC02-76SF00515). A.S. acknowledges partial support by the Feodor-Lynen program of the Alexander von Humboldt Foundation. Work by D.B. and T.J.S. was performed under the Partnership Program of the Materials Innovation Institute M2I and the Foundation of Fundamental Research on Matter (F71.4.15562a), Netherlands Organisation for Scientific Research. This work used the Stanford Nano Shared Facilities, supported by the NSF (ECCS-1542152).


Keywords: halide double perovskite, band gap, absorber, band structure, doping
Mind the gap: Unlike in ABX$_3$ perovskites (X = halide), the bandgap transition in A$_2$BB'X$_6$ double perovskites has substantial metal-to-metal (B to B') charge-transfer character, which allows us to access small bandgaps by aligning the energies of the B-site metal frontier orbitals.

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