Guanidinium and Mixed Cesium–Guanidinium Tin(II) Bromides: Effects of Quantum Confinement and Out-of-Plane Octahedral Tilting

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Supporting Information

ABSTRACT: Hybrid organic–inorganic main-group metal halide compounds are the subject of intense research owing to their unique optoelectronic characteristics. In this work, we report the synthesis, structure, and electronic and optical properties of a family of hybrid tin (II) bromide compounds comprising guanidinium [G, C(NH₂)₃⁺] and mixed cesium–guanidinium cations: G₂SnBr₄, CsGSnBr₄, and Cs₂GSn₂Br₇. G₂SnBr₄ has a one-dimensional structure that consists of chains of corner-sharing [SnBr₅]²⁻ square pyramids and G cations situated in between the chains. Cs⁺ exhibits a pronounced structure-directing effect where a mixture of Cs⁺ and G cations forms mono- and bilayered two-dimensional perovskites: CsGSnBr₄ and Cs₂GSn₂Br₇. Furthermore, the flat shapes of the guanidinium cations induce anisotropic out-of-plane tilts of the [SnBr₆]⁴⁻ octahedra in the CsGSnBr₄ and Cs₂GSn₂Br₇ compounds. In G₂SnBr₄, the Sn lone pair is highly stereoactive and favors non-octahedral, that is, square pyramidal coordination of Sn(II). G₂SnBr₄ exhibits bright broad-band emission from self-trapped excitonic states, owing to its soft lattice and electronic localization. This emission in G₂SnBr₄ is characterized by a photoluminescence (PL) quantum yield of 2% at room temperature (RT; 75 ± 5% at 77 K) and a fast PL lifetime of 18 ns at room temperature.

Hybrid organic–inorganic tin (II) halide compounds are intensely researched due to their photophysics and electronic properties, which are all governed by the structural diversity of Sn(II) halide anionic networks.¹–⁶ Such compounds are promising for application in light-emitting devices,⁶–⁸ solar cells,⁹,¹⁰ and photodetectors.¹¹ The crystal structure of hybrid tin (II) halide compounds consists of Sn(II)X (X = Cl, Br, I) coordination anionic networks and organic cations. Sn(II)X units can arrange themselves into a vast variety of structures: from extended three-dimensional (3D) structures composed of Sn(II)X coordination polyhedra connected by corners, edges, and faces to isolated polyhedral units (0D compounds) with a plethora of structures in between.¹,³,¹²–¹⁶ The Sn(II)-X units thus far observed experimentally include trigonal pyramids (coordination number, CN, of 3),¹⁷,¹⁸ seesaws (CN = 4),⁶ square pyramids (CN = 5),¹⁹,¹⁰ and, most commonly, octahedral units (CN = 6).¹,²⁰ The coordination geometry of the Sn(II) ion is a complex interplay that involves the effects of the stereoactivity of the 5s lone pair as well as the geometry of the organic cation and the interactions of the cation with inorganic...
units such as hydrogen bonding. Satisfactory rationalization (and prediction) of these effects on the atomistic and electronic structure of the resulting compounds remains a formidable challenge.

The electronic band structure of hybrid Sn(II) halide compounds at the band gap is formed mainly by Sn 5p and 5s orbitals and halide np orbitals. Nonconjugated organic amines do not significantly contribute to frontier orbitals. In hybrid tin (II) halide perovskite structures, such as (CnH2n+1CH2NH3)nSnI3, the ns2 pair of Sn defines an antibonding character of the valence band maximum by coupling with the p orbitals of halogen atoms. The band gap depends on the dimensionality and connectivity of the Sn(II)-X units, the atomic number of the halogen, and distortions of the metal halide polyhedra (governed by the organic moiety). For instance, the optical band gap of 3D CH3NH3SnI3 is 1.26 eV, whereas 2D [C6H5CH2CH2NH3]2SnI4 has an optical absorption edge at 1.97 eV.24

In the context of real-world applications, low-dimension hybrid Sn(II) halides might eventually be of use as bright light emitters for lighting and other applications. For instance, 0D (CnH2n+1Br)nSnBr4 [organic cation is N,N'-dimethylethylen-1,2-diammonium] demonstrates bright, yellow, broad-band photoluminescence (PL) with a quantum yield (QY) of ~85% and a large Stokes shift (~100 nm) and a full width of half maximum (FWHM) ~ 126 nm.7 The corresponding compound, (CnH2n+1Br)nSnBr4 containing exclusively bromide exhibits a QY close to 100%7. The structure of these compounds comprises SnX6 octahedra isolated by organic cations. Such emission characteristics are attributed to the emission from so-called self-trapped excitons, which are characterized by high binding energies and a low probability of interaction with intrinsic defects.25 Self-trapped excitons form due to a combination of electronic localization of an electron–hole pair (exciton) and structural distortion that occurs fast upon photoexcitation (Figure 1f), which lead to a Jahn–Teller-like distortion in the excited state.26 Hybrid 0D main-group metal halides are characterized by a soft lattice, strongly favoring the formation of self-trapped excitons due to facile structural distortion (exciton–phonon coupling). Radiative relaxation of self-trapped excitons leads to broad-band emission with a large Stokes shift as reported recently for a wide range of Sn(II) and Sb(III) halides.12,29 In comparison, the emission from 3D CH3NH3SnI3 results from free-excitonic states, and the PL band is characterized by a small Stokes shift, a narrow full width at half-maximum (FWHM), and a fast radiative lifetime.12,29

Both organic and inorganic constituents determine the resulting crystal structure. Thus, organic cations such as formamidinium [CH(NH2)+, FA] facilitate the formation of the 3D perovskite network of FASnI3. However, the use of large cations, such as phenethylammonium [C6H5(CH2)2NH3]+, typically results in a layered structure. A cation that is only slightly larger than FA – guanidinium – forms a layered G2SnI4 perovskite crystal structure with corrugated Sn–I layers.30 Guanidinium is a highly symmetric molecule (D∞h) and a potential contributor of six hydrogen bonds. The G cation due to its larger-than-FA ionic radius destabilizes the 3D perovskite network of corner-shared Sn–X octahedra.31 Instead, G2SnBr4 forms a 3D network composed of Sn–I octahedra with mixed connectivity: corner- and face-sharing. The appealing attributes of the G cation are its high thermodynamic stability, strong hydrogen bonding capabilities, and high basicity with pKb = 13.6 due to resonance stabilization by 6–8 kcal/mol.32,33 In a G–Sn–Cl system, there are two known compounds: 1D G2SnCl4 and the 3D perovskite-like G3SnCl4.34,35 Unlike G2SnI4 where the building blocks are Sn–I octahedra, G2SnCl4 has square pyramidal Sn(II) surrounded by Cl ions. So far, no compounds have been reported in G–Sn–Br system.

Herein, we investigated the G–Sn–Br and mixed-cation Cs–G–Sn–X (X = Br, I) systems wherein the effect of the additional smaller cation on the obtained structure can be probed. In our study, we did not succeed in obtaining quaternary mixed Cs–G–Sn(II) iodides and instead observed known ternary G2SnI4 and CsSnI3 phases.56 Therefore, the focus has been on the bromide systems. We have synthesized G2SnBr4 (Figure 1a) and compared it to CsSnBr3, and subsequently explored mixed Cs/G phases. G2SnBr4 is a 1D luminescent...
compounds with broadband PL and a PLQY of 2% at RT. It is thermally stable up to 300 °C. Two layered perovskite compounds, CsG5SnBr7 (II) and Cs5G5SnBr7 (III), were obtained and characterized in terms of their crystal structure, electronic structure, and optical properties. They reveal significant quantum confinement and that the planar shape of the G cation induces significant structural and electronic anisotropy. We then compare these structural effects to those in homologous lead-based compounds.

### METHODS

**Chemicals, reagents and synthetic procedures.** Guanidinium carbonate (G2CO3, >99%), hydrobromic acid (HBr, 48% water solution), and Sn powder (99.8%, ~325 mesh) were purchased from Acros. Cesium bromide (CsBr, 99%) and hydroiodic acid (HI, 57% water solution stabilized with 1% hypophosphorous acid, H3PO2) were obtained from ABCR. Tin (II) bromide (SnBr2, 99.2%) was obtained from Alfa Aesar. All chemicals were used as received without further purification.

All syntheses and further manipulations with the products were performed under inert conditions (argon or nitrogen atmosphere) using the Schlenk technique. Temperatures of the syntheses, stated below, correspond to the temperatures of the glycerol bath used as a source of heat. The syntheses were conducted in 10−20 ml Schlenk vessels equipped with a stirring bar.

G2SnBr4 (I) was crystallized from HBr. Briefly, 0.250 g (2.1 mmol) of Sn powder was dissolved in 3 mL of HBr (degassed under stirring in an Ar atmosphere for ~20 min before hand); this mixture was stirred for 10 min at RT and then heated in the glycerol bath at 85−90 °C. When all of the Sn was dissolved, 0.378 g (2.1 mmol) of G2CO3 was slowly added. Strong evolution of gas was observed (CO2). The reaction mixture was then stirred for an additional 5 min resulting in a clear colorless solution, whereupon the stirring and the heating were discontinued. Colorless transparent needles crystallized upon cooling and were separated by vacuum filtration under Ar flow. The product was dried under vacuum at 65−70 °C for 6 h. Yield: 41% (with regard to the initial Sn).

CsG5SnBr7 was synthesized from stoichiometric quantities of Sn and CsBr precursors in HBr. Briefly, 0.180 g (1.5 mmol) of Sn was dissolved in 3 mL of HBr as described above. Next, 0.320 g (1.5 mmol) of CsBr was added, and a black precipitate formed immediately. A mixture was stirred for an additional 5 min at 105 °C. Further manipulations with the product were identical to those with G5SnBr7.

For the preparation of Cs5G5SnBr7 (III), 0.107 g (0.9 mmol) of Sn powder was dissolved in 3 mL of HBr, stirred for 10 min at RT, and then heated to 85−90 °C. When all of the Sn was dissolved, 0.486 g (2.7 mmol) of G2CO3 and 0.1915 g (0.9 mmol) of CsBr were slowly added. Strong evolution of gas (CO2) was observed, and a black precipitate formed. The reaction mixture was stirred and kept at 85−90 °C for ~5 min until a slightly yellowish solution was obtained. Next, the stirring and heating were discontinued, and the mixture was cooled down under a stream of cold tap water. Initially, some black precipitate of Cs5SnBr7 crystallized out (Figure S1). In a few minutes, red crystals started appearing, and the black powder dissolved. The mixture was left to further crystallize for 1 week. Finally, the red product was separated by vacuum filtration under an inert atmosphere and dried under vacuum at 65−70 °C for 6 h.

Cs5SnBr7·1.5H2O, was crystallized from a solution of hot HI and HBr acids under N2. CsBr (0.500 g, 2.350 mmol) was first dissolved in HBr (4.0 mL) and HI (1.0 mL) solution in a 10 ml Schlenk reaction tube and sparged with N2 while stirring at RT for 30 min. SnBr2 (0.111 g, 0.399 mmol) was then added, and a black precipitate formed. This mixture was then heated with a glycerol bath until an orange solution was obtained (110 °C). The stirring and heating were discontinued, and the solution was cooled to RT. Within 1 h, orange needles crystallized out. The product was left to further crystallize overnight. The product was separated by vacuum filtration under N2 and dried overnight under vacuum at 70−80 °C. A yield of 50.8% was estimated relative to initial Sn.

**Characterization.** Powder X-ray diffraction (XRD) patterns were collected in transmission mode (Debye−Scherrer Geometry) with a STADIP diffractometer (STOE& Cie GmbH) equipped with a curved Ge (111) monochromator (CuKα = 1.54056 Å) and a silicon strip MYTHEN 1K Detector (Fa. DECTRIS). Rietveld refinement was performed using the FullProf Suite.35 A ground powder was placed between adhesive tape (for G5SnBr7 and CsG5SnBr7) or sealed in a 0.1 mm glass capillary (for G2SnBr4 and CsSnBr3). Single-crystal XRD measurements were conducted on a Bruker Smart Platform diffractometer equipped with an Apex I CCD detector and a molybdenum (MoKα = 0.71073 Å) sealed tube as an X-ray source. Crystals were tip-mounted on a micromount with paraffin oil. The data was processed with the APEX3 software package,36 and the structure solution and refinement were performed with SHELXL and SHELXLE,37 respectively, which are embedded in Olex2.38 The crystal structures were solved with direct methods, light elements (C, N) were located in the difference Fourier map, and hydrogen atoms were placed at calculated positions. The crystallographic data for the reported tin halide compounds were deposited at the Cambridge Crystallographic Data Centre (CCDC) under the codes 1854819 (G2SnBr7), 1854833 (CsG5SnBr7), and 1854838 (CsG5SnBr7), as well as at the Inorganic Crystal Structure Database (ICSD), that is, card number 434800 for CsSnBr3.39 UV−Vis diffuse reflectance spectra of the microcrystalline powders were collected using a Jasco V670 spectrophotometer equipped with a deuterium (D2) lamp (100−360 nm) for use in UV and a halogen lamp (330−2700 nm) for use in UV/NIR, and an integrating sphere detector (ILN-725) with a working wavelength range of 220−2200 nm. The diffuse reflectance data were transformed with the Kubelka−Munk model into the absorption/scattering ratio spectrum. Photoluminescence spectra were measured with a CCD fiber spectrometer (LRI, Aesq Instruments) with a 355 nm excitation source (frequency-tripled, picosecond Nd:YAG laser, Duetto from Time-Bandwidth). PL emission from the samples was passed through a long-pass optical filter with an edge at 400 nm to reject the excitation laser line. PL spectra were corrected to the spectral sensitivity of the detection system. For temperature-dependent PL measurements, a sample of CsSnBr3 was placed atop of a four-stage Peltier cooling/heating element in an evacuated chamber with a quartz window. The sample temperature was adjusted and stabilized with an accuracy of 0.25 °C by a homemade electronic scheme based on an Arduino microcontroller and thermocouple sensor. The current through the Peltier system was reversible, thus the setup provided a wide working temperature range of −40 to 120 °C. This is an open-source project by the authors, deposited and described in details at https://www.researchgate.net/project/High-power-thermoelectric-cooler-TEC-controller-with-4-stage-Peltier-refrigerator-heater. Time-resolved photoluminescence (TR-PL) measurements were performed using a time-correlated single-photon counting (TCSPC) setup, equipped with an SPC-130-EM counting module (Becker & Hickl GmbH) and an IDQ-ID-100-20-ULN avalanche photodiode (Quantumite) for recording the decay traces. The average radiative lifetimes were determined as 1τ = τ2 = τ3 = τ4, where τ1, τ2, τ3, and τ4 are the corresponding amplitudes and exponential decay parameters in the biexponential analysis. For measurements of PL and PLE spectra at low temperatures (77 K), the sample was encapsulated in a quartz tube filled with Ar gas and placed in a homemade cryostat. Low-temperature (77 K) and RT absolute PLQY values were measured with excitation at 340 nm using Quantaurus-QY spectrometer from Hamamatsu. The sample was encapsulated in a quartz tube filled with Ar gas. PL measurements at lower temperatures (in the case of Cs5G5SnBr7), down to 5 K, were conducted in a helium cryostat, and PL spectroscopy was performed by exciting the sample with a frequency-doubled Ti:Sapphire mode-locked laser delivering pulses of ~150 fs duration at 400 nm and a repetition rate of 80 MHz. The time-integrated PL was analyzed in a CCD-coupled grating spectrometer, whereas TR-PL traces were recorded with a streak camera. Thermal analysis [thermogravimetry (TG) and differential scanning calorimetry (DSC)] was performed using a Netzsch simultaneous thermal analyzer (STA 449 F5 Jupiter). A powdered
A sample of G2SnBr4 (21.9 mg) was placed in an alumina crucible (without a lid) and heated under Ar gas flow (50 mL/min) to 850 °C (10 °C min−1). Scanning electron microscopy (SEM) was carried out on a Quanta 200F microscope (Thermo Fisher Scientific) operated at an acceleration voltage of 20 kV. Energy-dispersive X-ray spectroscopy (EDXS) was performed with an Octane SDD detector (EDAX, Ametek) attached to the microscope column. For spectra recording and quantification (ZAF correction), the software Gemini (EDAX) was used.

**RESULTS AND DISCUSSION**

All presented compounds were crystallized from hydrobromic acid (HBr, 48% water solution) under an argon atmosphere using Sn powder, CsBr, and G2CO3 as precursors. G2SnBr4 (I), obtained from stoichiometric quantities of G and Sn(II), crystallizes as colorless transparent needles. Compound I was then characterized by single-crystal XRD (Figure 1a,b, Figure S2, and Tables S1−S4) and found to crystallize in the orthorhombic crystal system, space group Pna21. This structure consists of corrugated chains oriented along [010] (i.e., extended in the b direction), comprising corner-sharing square pyramids, [SnBr5]2−. The formation of such pyramids emphasizes the stereoactivity of the lone pair of Sn(II). The G cations are situated in the space between the chains and connect them via hydrogen−halogen bonds into a 3D supramolecular structure (Table S2). Two non-equivalent pyramids can be identified, which connect in an alternating manner. In both kinds of pyramids, Sn atoms are displaced out of the basal planes (by 0.23 and 0.24 Å, for Br1Br2Br5Br4 and Br2Br5Br8Br7 planes, respectively).

Figure 2. (a) Electronic band diagram of G2SnBr4 (I) computed by DFT. No dispersion can be observed except in the direction of the 1D chains [010] (Γ → Y, R → U, and Z → T paths). The space group Pna21 is a polar space group. Therefore, a Rashba splitting of the band edge states is predicted both in the conduction and valence bands away from the Y, R, and T critical points of the Brillouin zone. (b) Representation of the electronic densities of the conduction (red) and valence (blue) edge states.

Figure 3. (a) Crystal structure of cubic 3D-perovskite CsSnBr3. (b, c) Crystal structure of 2D perovskites: CsGSnBr4 (II) and Cs2GSn2Br7 (III). (d) Kubelka-Munk function of CsSnBr3 and III at RT. (e) Selected low-temperature PL spectra of III. (f) Selected low-temperature time-resolved PL spectra of III.
respectively, Figure 1b). The Sn–Br bond lengths are in the range of 2.724(2)–3.117 Å, which is comparable to the distances found in (NH4)2SnBr4·H2O (2.623–3.047 Å), where Sn(II) has the same square-pyramidal coordination.47 The shortest Sn–Br bond is with the Br ion at the apex of the pyramid. G3SnBr5(I) has a similar crystal structure to G3PbBr6, which contains an alternating orientation of [PbBr6]2− square pyramids in 1D chains.38 The 1D character is confirmed by inspection of the DFT electronic structure (Figure 2). Indeed, the band diagram (Figure 2a) exhibits an indirect band gap of 3.12 eV, and no dispersion of the edge state bands is observed except when following a path corresponding to the [010] crystal direction. Furthermore, the computed electronic edge state densities exhibit sizeable overlaps but only along the b crystallographic direction (Figure 2b), thus confirming the 1D character of the density of states close to the band gap. It is also worth noticing that Rashba splitting of the band edge states is worth noticing that Rashba splitting of the band edge states is strongly observed even when following a path corresponding to the [010] crystal direction.

By comparing the experimental powder XRD patterns with those simulated from single-crystal XRD data obtained herein (except for CsSnBr3, where ICSD card 4071 was used), I and CsSnBr2 were determined to be phase-pure (Figures S7 and S8). CsSnBr2 also appears to contain amorphous CsSnBr3 (Figure S8), which can explain the partially resolved component at 650–700 nm in the PL spectrum (Figure 1d). We then obtained two mixed guanidinium–cesium tin bromides: CsG3SnBr4 (II, orange-colored) and CsG3SnBr5 (III, red-colored), as a mixture of crystals. Both compounds are layered perovskites (Figure 3b,c). The formation of these phases was found to be in strong competition with the crystallization of compounds I and CsSnBr2. Cs3G3SnBr2 (III) was obtained as the dominant phase, with Cs3SnBr2 (II) as a major impurity (below 10%, Figure S9) at a molar ratio of Cs/G/Sn = 1/6/1. Optical absorption analysis of the sample of Cs3G3SnBr2 by a Kubelka–Munk function points to a possible trace quantity of rather amorphous CsSnBr3, thus giving rise to a small shoulder in the 650–700 nm region (Figure 3d). Both II and III crystallize in the orthorhombic crystal system, namely in Imma (II) and Cmmm (III) space groups, respectively (Figure 3b,c and Table S1). The crystal structures of II and III consist of 2D perovskite layers of corner-sharing [SnBr6]2− octahedra that are separated by cesium and guanidinium cations. The derivation of these structures can be visualized by cutting the parental cubic CsSnBr3 perovskite lattice along the (100) crystallographic plane and adding the octahedral tilting discussed later in detail). The importance of the mixed-cation design for obtaining 2D perovskites had been previously reported for the analogous CsGPbBr2 and CsGPbBrI compounds.40 Compound II contains monolayers of corner-sharing octahedra (Figure 3b), whereas compound III features double layers, connected via corners (Figure 3c). To the best of our knowledge, this is the first tin bromide featuring multilayers. The perovskite slabs are mutually shifted in-plane by a vector a/2 (a being an ideal cubic cell vector, Figure 3c). Cs+ and G cations in II and III are both situated in the interlayer space and alternate with each other in a periodic manner. In Cs3G3SnBr2 (III), cesium cations also fill the voids within the perovskite layers. G forms hydrogen bonds with the bromide ions from the perovskite layers (Tables S8 and S9). G cations are closely packed with intermolecular d(C···N) distances of ~3 Å. Due to the difference in ionic radii of Cs+ and G cations and the planar shape of the latter, Sn–Br octahedra are tilted in an alternating manner along the crystallographic axes b and c for II (Figure 3b) and III (Figure 3c, left), respectively. This generates smaller cavities for Cs+ and large voids for G cations. However, in the in-plane direction (for instance, along the crystallographic axis a for III, Figure 3c, right) the planar shape of the G cation and small atomic radius of Cs+ lead to the absence of steric strain with almost perfectly collinear Sn and Br atoms and subsequently longer Sn–Sn distances (6.011 Å) for II and III, respectively. This might contribute to an observed disorder in atomic positions of bromide along this direction. In Cs3SnBr4 (II), d(Sn–Br) = 2.909(2)–3.006(1) Å, which is comparable to Sn–Br distances in a CsSnBr3 cubic phase d(Sn–Br) = 2.898 Å.49 Sn–Br–Sn angles are in the range of 155.9(5)–180.0(6)° (Figure S10). Cs3SnBr2 and CsGPbBr2 both crystallize in the space group Imma and are isotypic.48 III is isotypic to CsG3PbBr2 and crystallizes in the space group Cmmm.41 The average Sn–Br distances for III are in the range of 2.915–2.987(1) Å (for additional crystallographic data for II and III, see Tables S10–S13). The interlayer Br–Br distances along the stacking direction (c and b for II and III, respectively)
are rather short: \(d(\text{Br}--\text{Br}) = 4.161 \text{ Å}\) in CsGPbBr\(_4\) (II) and \(d(\text{Br}--\text{Br}) = 4.070 \text{ Å}\) in Cs\(_2\)GSnBr\(_3\) (III).

In 3D perovskites, the critical point of the Brillouin zone where a direct band gap is observed is either the R point,\(^5\) for the cubic \(Pm-3m\) phase, or the Z point for the distorted tetragonal \(P4/mnm\) phase (Figure S11). In both cases, the critical wave vectors have the point symmetries of their respective lattices (\(m\)-\(3m\) and \(4/mmm\)). Similar symmetry considerations lead to critical wave vectors located along the stacking directions at the \(X(0,0,1)\) and \(Y(0,1,0)\) high-symmetry points for II and III, respectively, in the \(Imma\) and \(Cmmm\) Brillouin zones (both with point groups \(mmm\)). However, DFT simulations (Figure 4a,c) show that the electronic band gaps are predicted to be directly at the R \((0.5,0,0.5)\) and S \((0.5,0.5,0)\) points of the Brillouin zones of II and III, respectively. In both cases, the point symmetry of the critical wave vector is reduced from \(mmm\) to \(2/m\). This can be related to the anisotropy of the out-of-plane octahedral tilts, which is directly induced by the shape of the G cations. The octahedral tilting is clearly apparent for \(b(c)\) crystallographic planes (Figure 3b,c). The difference between II and III lies in the fact that the \((b,c)\) plane contains the stacking axis along \(c\) for II and along \(b\) for III. Furthermore, due to lattice distortions, the periodicity of the electronic density is doubled along \(b\) (\(c\)) for II (III), in contrast to the \(a\) direction. In turn, the valence band maxima and the conduction band minima show different hybridizations along all three directions (Figure 4b,d and Figure S12) as well as different band dispersions (Figure 4a,c). Both compounds II and III exhibit flat dispersions along the stacking axis despite the short Br–Br distances, a characteristic feature of 2D systems.

Analogous to CsSnBr\(_3\) (Figure S11) and contrary to I (Figure 2), the band gap remains direct in both II and III (Figure 4a,c) with a systematic decrease of the band gap values with the decrease of dimensionality and thickness of perovskite layers. These variations in DFT band gap energies (Table S14) are related to the equivalent quantum well thickness \((n = 1, 2, or \infty)\), which is roughly doubled when going from CsGSnBr\(_3\) (II) to Cs\(_2\)GSnBr\(_3\) (III) as a result of quantum confinement.

To experimentally probe the energy band gaps in these hybrid tin bromide compounds, an optical absorption analysis by means of a Kubelka–Munk function and PL measurements were performed (Figures 1c,d and 3d,e). The Kubelka–Munk absorption representation was derived from the diffuse reflectance spectra of powdered samples and was estimated as \(F(R_\infty) = \alpha/S = (1 - R_\infty)^2/2R_\infty\) \([F(R_\infty)]\) is the Kubelka–Munk unit, \(\alpha\) is the absorption coefficient, \(S\) is the scattering coefficient, and \(R_\infty\) is the reflectance of an infinitely thick layer. Here, we neglected the influence of excitonic effects on the absorption, because the excitonic band cannot be consistently resolved for all compounds and thus correctly deconvoluted from the band gap absorption edge. Hence, the band gap can be slightly underestimated. The optical band gap energies for I, III, and CsSnBr\(_3\) were determined by plotting \([F(R_\infty)\cdot h\nu]/(h\nu)\) versus \((h\nu)\) \((h\nu\) is the incident photon energy, \(r = 2\) for a direct band gap semiconductor, and \(r = 1/2\) for an indirect band gap semiconductor; Figure S13a,b). The highest absorption edge energy \((ca. 3.11 \text{ eV})\) was found for G\(_2\)SnBr\(_4\) (I) (Figure 1c), which is in agreement with its lowest electronic dimensionality (1D). The 3D cubic CsSnBr\(_3\) has the smallest band gap energy \((1.74 \text{ eV}, in\ agreement\ with\ the\ literature\)\), whereas 2D
CsSnBr₃ (III) has an intermediate band gap value of 2.16 eV (Figure 3d). Compound II could not be obtained in the phase-pure form needed for diffuse reflectance (only individual small crystallites could be selected for single-crystal XRD analysis). However, the visual appearance of II pointed towards an expected higher band gap in comparison to III (orange vs red). Despite the well-known underestimation of band gaps, such a decrease is predicted from DFT calculations (Figure 4 and Table S14) with 1.04 eV for II and 0.84 eV for III. CsGPbBr₃ has a larger optical experimental band gap than III, by 0.44 eV (2.60 eV vs 2.16 eV). A similar scenario was observed for the pair of (C₆H₄(C₆H₄NH₃)₃SnBr₄ (2.5 eV optical band gap) and its lead analogue (2.9 eV)). This might be a result of the difference in the E₂ ionization energies between tin and lead [E₂(Pb) = 31.94 eV and E₂(Sn) = 30.5 eV], the effect of the additional polarizability (presence of filled diffuse d and f orbitals below the valence electrons in Pb), and the distortions of the M–X (M = Sn, Pb) octahedra. A different degree of tilting of the MBr₆ octahedra is observed for CsGPbBr₃ and III (Figure S14), with stronger deviations from the ideal 180° for the lead compound. Interestingly, despite the different tilts of the octahedra, the angles are in the end compensated for in a manner that gives the required amount of space for guanidinium and cesium cations.

Both CsSnBr₃ and I are luminescent at RT, unlike II and III. The PL of G₃SnBr₄ (I) at RT is characterized by a broad emission band (Figure 1d) with a FWHM of ~121 nm, 2% PLQY, and a large Stokes shift of ~208 nm. At 77 K, the PLQY reaches 75 ± 5% and the PL band narrows down (FWHM ~72 nm) while retaining the same peak position at 557 nm with a Stokes shift of 233 nm. Additionally, the PL excitation spectrum at 77 K is blue-shifted compared to that at RT. CsSnBr₃ exhibits a PL maximum at 1.70 eV (Figure 1d) at RT, which is consistent with the literature value. In the PL spectrum of CsSnBr₃, a shoulder was observed at the higher energy side, which seems to originate from an amorphous or nanocrystalline CsSnBr₃ impurity. A blue shift of the emission bands of CsSnBr₃ was observed when the temperature increased from 228 to 383 K (Figure S15). This trend is consistent with previous temperature-dependent PL theoretical and experimental studies and is explained by the lattice expansion upon heating and local displacements of the Sn(II) cation. Large differences in the width of the PL bands and Stokes shifts for G₂SnBr₄ (I) and CsSnBr₃ indicate different radiative processes in these compounds. Time-resolved PL measurements (Figure 1e) yielded a PL lifetime of 0.4 ns for CsSnBr₃ and 18 ns in compound I. The short lifetime, the small Stokes shift, and the large Stokes shift and broader FWHM point to emission via self-trapped excitons with the PL lifetime.

For II and III, which are structurally more rigid and exhibit a delocalized electronic structure that reduces the propensity to form self-trapped excitons, the PL was measurable only at cryogenic temperatures (5–120 K, Figure 3e). At 5 K, the main band peaks are at 517 nm with an additional emission band around 577 nm. A broad emission band above 700 nm is also visible. Due to the very low PLQY and presence of different phases within the same sample, it is difficult to draw solid conclusions. Yet, one can attribute the main emission bands to free excitons or self-trapped excitons with low stabilization energy (due to hindered structural distortion as compared to 0D and 1D compounds). Finally, the lowest energy band might stem from surface defects. By increasing the temperature, the PL intensity quickly drops due to the activation of nonradiative processes. We have performed time-resolved PL measurements with a streak camera system, and the results are displayed in Figure 3f. The measured sub-100 ps decay times and their dependence on temperature attest to the presence of non-radiative processes, which efficiently quench radiative recombination.

In conclusion, we presented a highly luminescent 1D compound G₂SnBr₄ at 77 K, as well as layered 2D perovskites CsSnBr₃ and Cs₂GSnBr₇. In G₂SnBr₄, the Sn(II) lone pair is stereoeactive and influences the coordination environment of Sn(II). G₂SnBr₄ is a luminescent compound with broadband emission from self-trapped excitonic states that are enabled by the soft lattice and electronic localization. This emission is characterized by a PLQY of 2% at RT and 75 ± 5% at 77 K. G₂SnBr₄ does not thermally decompose until 300 °C. The addition of cesium to the G–Sn–Br system promotes the formation of structurally more rigid, layered perovskite compounds, obscuring the formation of self-trapped excitions but leading to a delocalized electronic structure. Cs₂GSnBr₇ has a smaller band gap than its lead analogue, CsGPbBr₃, due to the difference in E₃ ionization energies of tin and lead, higher electronegativity of Pb, and the different degree of structural distortion. Lastly, in-plane electronic coupling is anisotropic as a result of the planar shape of the guanidinium cation, which leads to significant octahedral out-of-plane tilting in only one of the two directions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemistry.9b00038.

Crystallographic details of G₂SnBr₄ (CIF)
Crystallographic details of Cs₂GSnBr₇ (CIF)
Crystallographic details of CsSnBr₃ (CIF)
Crystallographic details of Cs₂GSnBr₇ (CIF)

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Notes
The authors declare no competing financial interest.

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