Highly Emissive Self-Trapped Excitons in Fully Inorganic Zero-Dimensional Tin Halides

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Abstract: The spatial localization of charge carriers to promote the formation of bound excitons and concomitantly enhance radiative recombination has long been a goal for luminescent semiconductors. Zero-dimensional materials structurally impose carrier localization and result in the formation of localized Frenkel excitons. Now the fully inorganic, perovskite-derived zero-dimensional SnIV material Cs4SnBr6 is presented that exhibits room-temperature broadband photoluminescence centered at 540 nm with a quantum yield (QY) of 15 ± 5%. A series of analogous compositions following the general formula Cs4xAxSn(Br1_yIy)6 (A = Rb, K; x ≤ 1, y ≤ 1) can be prepared. The emission of these materials ranges from 500 nm to 620 nm with the possibility to compositionally tune the Stokes shift and the self-trapped exciton emission bands.

Interest in low-dimensional metal halide semiconductors,[1] and ultimately their zero-dimensional (0D) counterparts,[2] has been spurred by the increasing interest in 3D lead halide perovskites.[3] In recent years, lead halide perovskites have risen to prominence in the field of optoelectronics with their use in full-color imaging,[4] photodetection,[5] X-ray imaging,[6] hard-radiation detection,[7] solar cells,[8] and light-emitting diodes,[9] owing to their defect-tolerant photophysics and electronic trapping processes that are inherent in electronically extended (higher-dimensionality) solids, favors radiative recombination. Previously, the spatial confinement of carriers in 3D perovskites has been attained through crystal size control at the nanoscale (that is, top-down and bottom-up synthesis of nanocrystals).[10] In the case of 0D materials, such elaborate crystal size engineering is not required as the optical properties are instead governed by their structural dimensionality. Highly localized Frenkel-like excitons are formed instead of Wannier–Mott type excitons.

The library of 0D metal halides with octahedral building units includes both lead-based and lead-free compounds: TiIV, HfIV, ZrIV, PbII, SnIV, TeIV, SbIII, TiIV, HfIV, ZrIV, PdIV, PbII, SnIV, TeIV, SbIII, and BiIII.[11] However, only several of these examples exhibit photoluminescence (PL) at room temperature (RT), and this emission is seldom characterized by a high PL quantum yield (QY). The first examples with high QYs in excess of 50% were demonstrated only recently: (C4N2H14Br)4SnBr6 (QY = 95% ± 5%) and (C6N2H4Br)3SnI6 (QY = 75% ± 4%).[12] Both structures are constructed from disconnected [SnX6]n− octahedra, separated by large organic cations with a distance of more than 1 nm between Sn2+ centers.

Given the high PL QY of these hybrid materials and their novel approach towards exciton localization, herein we chose to pursue fully inorganic analogues such as Cs4SnBr6. While several studies have reported on the structure and basic properties of Cs4SnBr6, none have observed PL at RT.[12] Recently, calculations have shown that the Cs4SnBr6 phase should have a band gap of 3.37 eV.[13] We prepared Cs4xAxSn(Br1_yIy)6 (A = Rb, K) materials using a simple solid-state heat-and-beat approach, characterized them structurally, and found them to be luminescent at RT.

According to the CsBr–SnBr2 pseudo-binary phase diagram (Figure 1a), CsSnBr2 melts incongruently and competes with the decomposition into the black CsSnBr3 and CsBr. Therefore, phase-pure CsSnBr2 cannot be obtained by cooling from a melt of this composition. Instead, solid pellets of a mixture of CsBr (4.5 equiv.) and SnBr2 (1 equiv.) were repeatedly heated to 350°C for 60 h and reground in a glovebox between heating cycles. The highlighted green region in Figure 1a represents the experimental conditions that were found to yield the purest materials, that is, at temperatures...
below the decomposition point of Cs₄SnBr₈ (Supporting Information, Figures S1, S2; Tables S1, S2). Single crystals of Cs₄SnBr₈ were obtained by tempering a solid pellet at 350°C. Cs₄SnBr₈ crystallizes in a trigonal crystal system (R₃̅c space group; Figure 1b; Supporting Information, Tables S3–S9), wherein [SnBr₆]⁺ octahedra are separated by Cs⁺ cations. The Cs⁺ cations occupy two distinct crystallographic positions (Supporting Information, Figure S3).

Unlike the isostructural Cs₄PbBr₈, which shows narrow excitonic PL only at low temperatures and at wavelengths < 400 nm,[16] Cs₄SnBr₈ exhibits broad-band green–yellow PL at RT from STEs (peak maximum at 540 nm, Figure 1c). Upon measuring the PL excitation (PLE) and absorption spectra it was found that Cs₄SnBr₈ resembled a molecular material with a sharp excitation peak at 340 nm yielding a large Stokes shift of about 1.2 eV (Supporting Information, Figure S4). A PLOY of 15 ± 5% was measured at RT. PLE and PL spectra were found to be tunable through the partial substitution of both A-site cations (Cs with Rb, K) and the halide anions (Br with I). Na was not observed to substitute Cs (Supporting Information, Figure S5).

In (C₃N₃H₆X)₄SnX₄ (X = Br/I),[21] the addition of iodide red-shifts both the excitation and STE emission spectra. Similarly, the PL of Cs₄SnX₄ shifts to 620 nm (orange emission) at a Br:I ratio of ca. 1:1 (Figure 2a). In agreement with Vegard’s law, a linear change in both the a and c lattice parameters was observed over the range of compositions from Cs₄SnBr₈ to Cs₄SnI₄ (Supporting Information, Figures S6, S7; Tables S10, S11). Samples with greater than 50% substitution by iodide, however, did not exhibit PL at RT and were not investigated further.

While bromide and iodide occupy the same general position within the structure of Cs₄SnBr₈, Rb⁺ and K⁺ could potentially substitute two distinct crystallographic positions of Cs⁺ (Supporting Information, Figure S3). Substitution by Rb⁺ or K⁺ occurred only on the Cs2 site (1/4 of all Cs six-fold coordination. Figure 2b; Supporting Information, Figure S8, Tables S12, S13), which explains the observed experimental 25%-limit for substitution (Supporting Information, Figure S9). Plotting the lattice constants against the molar fractions of K⁺ or Rb⁺ ions, estimated from Rietveld refinement and energy-dispersive X-ray spectroscopy (EDS), yields a seemingly linear trend for the c parameter, in agreement with Vegard’s law, whereas the a parameter increases only slightly (Figure 2c; Supporting Information, Figures S9–S11). The site affected is part of an infinite chain of [SnBr₆]⁺ octahedra separated by Cs/Rb/K ions. Since the chain is oriented parallel to the c-axis, substitution by Rb or K will cause the largest effect along this axis resulting in a decrease in the c parameter.

The substitution of Cs⁺ by Rb⁺ or K⁺ results in a blue-shift of the PL maximum. This shift is dependent on both the degree of substitution and on the identity of the substituting cation. For 25% substitution, Rb⁺ shifts the PL peak to 519 nm, whereas K⁺ yields a PL peak at 500 nm (Figure 2d). Strikingly, the PLE remains unaffected. The same scenario was observed for the other examined Br:I ratios (ca. 5:1, 2:1, 1:1; Figure 2e; Figure S12, Tables S14, S15).

Temperature-dependent PL spectra were measured down to 6 K (Supporting Information, Figures S13, S14). It was found that the PL intensity increased with decreasing temperature and, in the case of Cs₄SnBr₈, the emission intensity reached a maximum at about 200 K. Given a RT QY of 15 ±

**Figure 1.** a) The pseudo-binary CsBr–SnBr₃ phase diagram. The highlighted green region represents the experimental conditions found to yield the purest Cs₄SnBr₈ material. b) The crystal structure of Cs₄SnBr₈ viewed along the (111) axis with [SnBr₆]⁺ octahedra (gray with green bromine atoms) separated by Cs⁺ cations (blue). c) PL and PLE spectra for Cs₄SnBr₈ at RT.
5\%, the QY of Cs₄SnBr₆ is estimated to be near-unity at 200 K
(Supporting Information, Figure S15a). At 6 K, no higher-
energy emission, that is, from free excitons, could be observed
in Cs₄SnBr₆ or Cs₄SnBr₃I₃ (Supporting Information, Figures S14, S15b).

The time-resolved PL (TRPL) of Cs₄SnBr₆ at RT exhibits
a monoexponential decay with an average lifetime of 540 ns
(Supporting Information, Figure S16). TRPL decays were
then recorded at 200 K (the temperature that corresponds to
highest QY, Figure 2f; Supporting Information, Figure S15),
and it was observed that the lifetime increased to 1381 ns
(1424 ns for K-substitution), while remaining monoexponen-
tial (Figure 2f). Substitution with iodide accelerated the
average lifetime (600 ns at 200 K for Cs₄SnBr₃I₃, Figure 2f;
see the Supporting Information, Figure S16b for RT compar-
ison). Additionally, the radiative lifetime was found to be
insensitive towards dilution with CsBr, excitation intensity,
crystallinity, and encapsulation within a UV-curable epoxy
(Supporting Information, Figure S16c,d), indicating a lack of
surface effects on PL properties in these 0D materials.

Broad-band, strongly Stokes-shifted emission with rela-
tively long radiative lifetimes indicates the formation of STEs
(Figure 3a). As in molecular complexes and similarly small
entities, structural changes occur between the ground state
and the excited state. Emission from STEs is then somewhat
to an indirect-gap optical transition since coupling to
phonons is required. Besides 0D-tin halides, emission
from STEs has also been observed in 1D- and 2D-layered
materials.

To rationalize the effect of A-site substitution observed in
these materials, calculations of the partial density of states
(DOS) by density functional theory (DFT) were utilized
(Figure 3b; Supporting Information, Figure S17, Table S16).

A \(1 \times 1 \times 1\) unit cell (66 atoms) was used as a model system
for Cs₄SnBr₆, Cs₃K₀.₈SnBr₆, and Cs₄SnBr₃I₃ materials. The
electronic states were found to be highly localized in all three
compositions and the band gap was found to consist of Sn 5s,
Br 5p (conduction band/LUMO) and Sn 5p, Br 5p orbitals
(valence band/HOMO). A-cation orbitals do not significantly
contribute to HOMO and LUMO states (Supporting Infor-
mation, Figure S17). This is corroborated by the experiment
given that A-site substitution did not substantially affect the
PLE spectra.

It was previously shown that both tin- and lead-halide
octahedra distort significantly upon photoexcitation in low-
dimensional materials. By modeling the excited state and
ground state geometries, we find that the extent of distortion
was the principle reason for the Stokes shift (Figure 3b). A
pseudo-Jahn–Teller distortion was observed with elongation
of up to 17\% in the axial Sn–Br bonds, and a contraction of
up to 7\% in the equatorial bonds. This distortion was found to
be greatest in Cs₄SnBr₆ and decreased from Cs\(^{+}\) to Rb\(^+\) to K\(^+\).

Figure 2. Structural and optical characterization of Cs₄₋ₓAₓSn(Br,I)₆ compounds (A=K, Rb). a) PL and PLE spectra of Cs₄Sn(Br,I)₆. b) Crystal
structure of Cs₃K₀.₈SnBr₆ determined by Rietveld refinement. c) The change in the a and c lattice parameters upon Cs\(^ {+}\) substitution by Rb\(^+\) and
K\(^+\). d) PL and PLE spectra for Rb\(^+\) or K\(^+\) substituted compounds. e) Image of Cs₄₋ₓAₓSn(Br,I)₆ powders under 365 nm UV light. f) TRPL of
Cs₄SnBr₆, Cs₃K₀.₈SnBr₆, and Cs₄SnBr₃I₃ at 200 K.
Figure 3. a) Generic configurational coordinate diagram illustrating the origin of STE PL in Cs$_x$A$_{1-x}$Sn(Br$_x$I$_{1-x}$)$_4$. b) Ground-state and excited-state (STE) HOMOs and LUMOs. c) Experimental and theoretical results demonstrating that PL energy varies linearly with the ratio of c-axis to a-axis length. Variable-temperature measurements (three data points; black circles) are plotted for Cs$_5$SnBr$_6$ at 100 K, 200 K, and 273 K.

(Supporting Information, Table S17). In other words, the energy required for distortion correlates well with the measured Stokes shift. Larger distortion is allowed by greater distance between the octahedra; primarily along the c-axis. The ratio between the lengths of the c- and a-axes was found to correlate most strongly with PL energy, experimentally and in calculations (Figure 3c). On the other hand, isotropic changes to the unit cell (that is, contraction during cooling) do not affect the PL (Supporting Information, Table S18).

In summary, several new 0D tin halides with the general formula Cs$_x$A$_{1-x}$Sn(Br$_x$I$_{1-x}$)$_4$ have been found to exhibit broadband RT PL that is tunable from 500 nm to 620 nm. The PL peak position and Stokes shifts can be concomitantly adjusted by the substitution of Cs$^+$ with either Rb$^+$ or K$^+$ as well as Br$^-$ by I$. PL properties were rationalized by the DFT analysis of STEs. Future studies might concern applications of such materials in luminescent solar concentrators and light-emitting devices, harnessing their structural tunability and fully inorganic compositions.

Experimental Section

Materials and methods are included in the Supporting Information. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+ 49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-434641, 434642, 434643, 434644, 434645, 434646, and 434647.

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Conflict of interest

The authors declare no conflict of interest.

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