ABSTRACT: The vast structural and compositional space of metal halides has recently become a major research focus for designing inexpensive and versatile light sources; in particular, for applications in displays, solid-state lighting, lasing, etc. Compounds with isolated ns²-metal halide centers often exhibit bright broadband emission that stems from self-trapped excitons (STEs). The Sb(III) halides are attractive STE emitters due to their low toxicity and oxidative stability; however, coupling these features with an appropriately robust, fully inorganic material containing Sb³⁺ in an octahedral halide environment has proven to be a challenge. Here, we investigate Sb³⁺ as a dopant in a solution-grown metal halide double perovskite (DP) matrix, namely Cs₂MInCl₆ₙₓSb (M = Na, K, x = 0–100%). Cs₂KInCl₆ is found to crystallize in the tetragonal DP phase, unlike Cs₂NaInCl₆ that adopts the traditional cubic DP structure. This structural difference results in distinct emission colors, as Cs₂NaSbCl₆ and Cs₂KInCl₆:Sb compounds exhibit broadband blue and green emissions, respectively, with photoluminescence quantum yields (PLQYs) of up to 93%. Spectroscopic and computational investigations confirm that this efficient emission originates from Sb(III)-hosted STEs. These fully inorganic DP compounds demonstrate that Sb(III) can be incorporated as a bright emissive center for stable lighting applications.

Light-emitting ns²-metal halide-based materials have been the subject of continued interest over several decades, owing to the facile synthesis by wet and solid-state methods as well as their exceptional electronic and optical properties. The latter include narrowband and broadband emission for display technologies,¹−⁴ lasing,⁵−¹⁰ quantum light sources,¹¹−¹² solid-state lighting,¹³−¹⁵ scintillators,¹⁶ remote thermography,¹⁷ and luminescent solar light converters and concentrators.¹⁸−²⁰ The vast variety of luminescence characteristics arises from structural tunability. Metal halide polyhedral units as building blocks can form extended structures (e.g., APbX₃, A₂AgBIX₆, where A = monovalent cation, X = Cl, Br, I) with predominantly Wannier–Mott-type excitons,¹⁵−¹⁷ layered structures with both Wannier–Mott and Frenkel excitons,²¹,²² and fully isolated OD metal halides exhibiting characteristic broadband emission from self-trapped excitons (STEs) of Frenkel-type.²³ For generating STE emission in the visible region, the most suitable ns²-metals include Ge(II), Sn(II), Sb(III), and Te(IV), whereas Pb(II) and Bi(III) systematically display higher energy emission, often in the UV region.²¹−²³ In this work, we have concentrated our attention on the broad STE emission from Sb(III) due to its oxidative stability, in great contrast to the unstable oxidation states of Ge(II) and Sn(II). Organic–inorganic Sb(III) halide hybrids with various organic cations exhibit broadband and strongly Stokes-shifted emission in the yellow-red region with near-unity photoluminescence quantum yield (PLQY) at room temperature (RT).²⁴−²⁷ In contrast, the known fully inorganic Sb(III) compounds (e.g., Cs₅Sb₂X₉, Cs₂NaSbX₆)²⁸,²⁹ are nonemissive at RT, although they are much more desirable due to their higher thermal stability. Therefore, to achieve an efficient RT STE of Sb³⁺, we adopt an alternative strategy, namely, doping ns²-metal ions into a suitable inorganic halide matrix.¹⁰,³⁰ In this case, the doping level serves as a useful tuning knob for maximizing the emission intensity or preventing self-quenching at high concentrations. For example, the Sb³⁺ ions in Cs₂NaSbCl₆ fully quench each other at RT,³⁰ requiring the use of diluted Sb³⁺ systems for RT emission. The most suitable fully inorganic matrix has to provide an O₈-halide environment for Sb³⁺ and at the same time possess a wide optical band gap to prevent self-absorption. Doping on an isovalent host site is also advantageous, although examples of aliovalent Sb³⁺ doping are known.³¹ The matrix satisfying these requirements can be found among the halide elpasolites, also known as halide double perovskites (DPs).³² The structure of cubic elpasolites can be viewed as derived from a cubic perovskite structure AM³X₈ by the transmutation of a pair of M¹¹ sites into distinct M¹ and M¹¹ sites, resulting in an A₃M²⁺M¹¹X₈ stoichiometry. Although elpasolites are 3D structurally, in some compositions (where M¹ is an alkali halide metal), the orbital overlap...
between the nearest $[\text{M}^{III}\text{Cl}_6]$ octahedra is broken by the adjacent $[\text{M}^{I}\text{Cl}_6]$ octahedra, resulting in reduced electronic dimensionality.\textsuperscript{33} The emission of Sb$^{3+}$ dopant in some bulk halide DP ($\text{Cs}_2\text{NaMX}_6$, where M = Y, Sc, La and X = Cl, Br) was reported by Oomen et al. in the late 80s.\textsuperscript{34,35} These compounds exhibited emission centered in the range from 440 to 492 nm, depending on the size of the space available for the Sb$^{3+}$ ion. In this study, we have selected In$^{3+}$ as a trivalent cation due to its oxidative and photostability, as well as the large optical band gap of the resulting DP. In addition to Na$^+$, the larger K$^+$ was selected to fine-tune the Sb$^{3+}$ emission.

During the preparation of this manuscript, Zeng et al. also reported on Sb-doped $\text{Cs}_2\text{NaInCl}_6$.\textsuperscript{36} When suitably small amounts of Sb$^{3+}$ are doped into $\text{Cs}_2\text{NaInCl}_6$, the products retain the original structure, as confirmed by powder XRD (Figure S1). The peak positions shift linearly toward lower angles with increasing Sb$^{3+}$ content, indicating a larger unit cell in agreement with Vegard’s law (Figure S1b,c).\textsuperscript{37} This increase is the opposite of what is expected from the stated ionic radii of Sb$^{3+}$ (76 pm), which is smaller than In$^{3+}$ (80 pm),\textsuperscript{35} but is consistent with the larger lattice constant of $\text{Cs}_2\text{NaSbCl}_6$ (10.7780 Å) relative to that of $\text{Cs}_2\text{NaInCl}_6$.\textsuperscript{38} This disparity can be ascribed to the bond-destabilizing effect of the $n^2$ lone pair, as described for Bi$^{3+}$ by Shannon.\textsuperscript{37} To maintain an average cubic symmetry in $\text{Cs}_2\text{NaSbCl}_6$, the stereoeactivity of the lone pair must lead to a highly dynamic distortion of the SbCl$_6^{3-}$ octahedra.\textsuperscript{29} The bond-length increase also confirms that Sb$^{3+}$ substitutes into the In$^{3+}$ position of $\text{Cs}_2\text{NaInCl}_6$, as any substitution of Na$^+$ by the much smaller Sb$^{3+}$ ions would decrease the size of the unit cell. When 60% or more of Sb$^{3+}$ is added during synthesis, weak peaks characteristic of the $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ impurity phase start to appear.

Contrary to the sodium-containing DP, the $\text{Cs}_2\text{KInCl}_6:x\text{Sb}$ ($x = 0, 1, 5, 10, 15, 20, \text{and } 40\%$) compounds could be prepared only as fine powders, which were not suitable for single-crystal XRD. Powder XRD patterns of $\text{Cs}_2\text{KInCl}_6$ show doubled peaks near the strong reflections of the $Fm\overline{3}m$ cubic DP structure, indicating a structure of lower symmetry (Figure 1a,c). LeBail pattern matching using GSAS-II\textsuperscript{39} (Figure S2b) reveals that these compounds possess tetragonal symmetry, with the space group $I4/m$ and unit cell parameters $a = b = 16.9732(2)$ Å and $c = 10.9937(1)$ Å. This corresponds to a distorted DP structure (Figure S2a) due to the large size of the

![Figure 1](https://dx.doi.org/10.1021/acs.chemmater.0c01004)

Figure 1. (a) Comparison of $\text{Cs}_2\text{NaInCl}_6$ and $\text{Cs}_2\text{KInCl}_6$ crystal structures, experimental and simulated XRD patterns for (b) $\text{Cs}_2\text{NaInCl}_6$ and (c) $\text{Cs}_2\text{KInCl}_6$. (d) Images of $\text{Cs}_2\text{NaInCl}_6:1\%\text{Sb}$ crystals under visible light (Vis) and 365 nm UV excitation.

![Figure 2](https://dx.doi.org/10.1021/acs.chemmater.0c01004)

Figure 2. Typical PL (under 320 nm UV excitation) and PLE of (a) $\text{Cs}_2\text{NaInCl}_6:5\%\text{Sb}$ and (b) $\text{Cs}_2\text{KInCl}_6:5\%\text{Sb}$. (c) PLQY dependence on the concentration of the Sb$^{3+}$ dopant.
Cs2NaInCl6: increasing Sb3+ content. This phase conversion also alters the optical properties as the maximum of the emission shifts toward longer wavelengths, while the maximum of the PLE band has been ascribed to a dynamic Jahn–Teller distortion in the excited state.33 As demonstrated in Figure 2c, the amount of Sb3+ dopant strongly influences PLQY. The highest PLQYS were obtained for the Cs2NaInCl6:1%Sb and Cs2KInCl6:5%Sb structures (λexc = 320 nm) and were equal to 82 and 93%, respectively. A further increase of the doping level caused the self-quenching effect. Figure 3a shows the time-resolved PL decay curves of Cs2NaInCl6:1%Sb and Cs2KInCl6:5%Sb measured at 445 and 495 nm, respectively, at RT (λexc = 320 nm) and the corresponding time constants of the biexponential fit. (b) Experimental dependence of the PL peak broadening with temperature for Cs2NaInCl6:1%Sb and Cs2KInCl6:5%Sb. The experimental data are fitted with a model (solid line), from which the electron–phonon coupling strength (γELO) and optical phonon energies (ELO) are obtained.

Extended exposure of Cs2KInCl6:xSb to the acidic environment results in the incorporation of water molecules and the presence of the impurity phase Cs2InCl5:H2O (Figure S2c). This complicates the interpretation of the powder XRD, as there is no clear trend in the lattice parameters with increasing Sb3+ content. This phase conversion also alters the optical properties as the maximum of the emission shifts toward longer wavelengths, while the maximum of the excitation band remains unchanged (Figure S2d,e). Cs2NaInCl6:xSb samples exhibited no degradation upon storage in air for a few months, whereas with Cs2KInCl6:xSb, yellow-luminescent grains started to appear after a few weeks in air, indicating that the tetragonal structure may be metastable (Figure S3). Similar instability was observed for isostructural CsInCl3.28

Sb-doped Cs2NaInCl6 and Cs2KInCl6 samples exhibit broadband blue and green PL (Figure 2a,b), respectively, while the undoped Cs2NaInCl6 and Cs2KInCl6 compounds exhibited no visible PL at RT (Figure S4). This is in contrast to the study of Zeng et al.,36 who reported a PL band with a maximum at 445 nm for undoped structures. Sb-doped compounds also exhibit new bands in the absorption spectra corresponding to Sb states within the band gap of the Cs2MInCl6 matrix (Figure S5). As the PL intensities are low for the samples with high Sb3+ content due to self-quenching, we mainly analyzed the samples with Sb3+ concentration below 20%. For ns2 ions such as Sb3+, the ground state is denoted by the 1S0 atomic term, whereas the excited state (sp) splits into four energy levels, namely, 1P1, 3P0, 3P1, and 3P2. The 1S0−3P1 transition is partially allowed due to spin–orbit coupling for heavy atoms, while the 1S0−3P2 and 1S0−3P0 transitions are totally forbidden at the direct dipole transition level. The characteristic excitation band (commonly denoted as the A-band) with two maxima at 320 and 335 nm can be assigned to the 1S0−3P1 transition of Sb3+ (PLE maps are presented in Figure S6a,b). The split in the PLE band has been ascribed to a dynamic Jahn–Teller distortion in the excited state.34

The PL emission situated in the 380–700 nm range (with a maximum near 445 nm for Cs2NaInCl6:5%Sb and 495 nm for Cs2KInCl6:5%Sb) can be ascribed to the 3P1−1S0 transition, similar to the case of Cs2NaMCl6 (M = Sc, Y, La) matrices.34 The Stokes shift of Sb3+ luminescence, defined as the energy difference between the maximum of the excitation and emission bands, is equal to 110 and 160 nm for Cs2NaInCl6:5%Sb and Cs2KInCl6:5%Sb, respectively. The shape and maxima of the PL excitation (PLE) and PL spectra remain the same for different amounts of Sb3+ ions in the crystal structure (Figure S7a,b). The only exception is in the PL spectrum of Cs2KInCl6:1%Sb, where a shoulder was observed at low energy, which seems to originate from the Cs2InCl6·H2O:1%Sb impurity.
The $\Gamma_0$ is a temperature-independent inhomogeneous broadening, which is related to scattering due to disorder and imperfections. The second and third terms represent homogeneous broadening, resulting from scattering from acoustic and optical phonons. The last term accounts for the scattering of ionized impurities and does not contribute in the case of Cs$_2$MInCl$_6$: The optical phonon band structure with states originating mainly from the impurity ion Sb$^{3+}$.

The analysis of the DOS of the Sb-doped Cs$_2$NaInCl$_6$ with a cubic structure shows that the SbCl$_6$ HOMO appears above the host valence band while the SbCl$_6$ LUMO appears in a gap of the conduction band structure (Figures 4a and S9). The oscillator strength of the SbCl$_6$ HOMO--LUMO transition is much higher than those of the matrix, and therefore both optical excitation and emission are occurring between SbCl$_6$ states. The SbCl$_6$ HOMO has Sb-s and Cl-p character, whereas the LUMO consists of Sb-p and Cl-p orbitals. This can also be confirmed by calculating the SbCl$_6$ HOMO--LUMO difference, 3.92 eV, which is close to the experimental PLE peak at 12 K of 3.75 eV (Figure S10). For Sb-doped Cs$_2$KInCl$_6$, which has a tetragonal structure, the predicted SbCl$_6$ HOMO--LUMO gap is lower (3.73 eV) and better agrees with the experiment (Figure 4c). The calculations confirm that the observed luminescence mechanism does not involve states from the DP host, but both HOMO and LUMO are localized on the dopant sites, namely, SbCl$_6$ octahedra.

In summary, we have designed and synthesized Cs$_2$MInCl$_6$Sb (M = Na, K) phosphors with blue and green emission and PLQYs of 82 and 93%, respectively. Experimental and computational studies reveal that the optical properties originate from STEs localized on SbCl$_6$ centers. We demonstrate that the emission maximum of the Sb$^{3+}$ dopant can be tuned not only by exchanging the M$^{3+}$ cation, but also
the M⁺ cation. Replacement of the Na⁺ cation by the larger K⁺ cation causes structural changes due to the size of the cation, resulting in a shift from cubic to tetragonal symmetry. This change is reflected in the increase of the Stokes shift and electron–phonon coupling. We anticipate that such fully inorganic, thermally robust, and bright emitters will find applications in solid-state lighting as well as emerging niches such as remote thermography, scintillation, neutron detection, cathodoluminescence, etc.

## EXPERIMENTAL SECTION

The list of chemicals is available in the Supporting Information.

**Synthesis of Cs₂NaInCl₆:Cs₂SbCl₆ Powder.** 
Cs₂NaInCl₆:Cs₂SbCl₆ was synthesized from stoichiometric quantities of CsCl, NaCl, InCl₃, and SbCl₃ precursors in HCl. Briefly, 0.6 mmol of CsCl and 0.3 mmol of NaCl powders were dissolved in 4 mL of HCl under stirring in an 8 mL vial at 100 °C. Separately, stoichiometric amounts of SbCl₃ and InCl₃ were dissolved in 1 mL of HCl and heated at 100 °C. When all of the precursors were dissolved, both solutions were mixed together and immediate precipitation of the colorless product was observed. The as-obtained product was separated by filtration and dried in an air at 50 °C for 6 h. Reaction yield: 79%.

**Synthesis of Cs₂KInCl₆:Cs₂SbCl₆ Single Crystals.** 
Cs₂KInCl₆:Cs₂SbCl₆ was synthesized from stoichiometric quantities of CsCl, NaCl, InCl₃, and SbCl₃ precursors in HCl. Briefly, 0.6 mmol of CsCl, 0.3 mmol of NaCl, and stoichiometric amounts of SbCl₃ and InCl₃ were dissolved in 6 mL of HCl under stirring in a 12 mL vial and heated at 100 °C. When all of the precursors were dissolved, the temperature was decreased to room temperature and small crystals grew overnight. To ensure the total removal of surface-adsorbed ions, the tiny crystals were rinsed with fresh HCl. The crystalline product was dried in the air at 50 °C until the weight of 5 mmol of Cs₂KInCl₆:Cs₂SbCl₆ Single Crystals. 

**Characterization.** Powder XRD patterns were collected in transmission mode (Debye–Scherrer Geometry) with an STADI P diffractometer (STOE & Cie GmbH) equipped with a curved Ge(111) monochromator (Cu Kα = 1.54056 Å) and a silicon strip MYTHEN 1K detector (Fa. DECTRIS). For the measurement, the ground powder was placed between adhesive tape, with the exception of Cs₂KInCl₆, which was measured in a Mark-tube capillary of 0.1 mm diameter. Single-crystal XRD measurements were conducted on a Bruker Smart Platform diffractometer equipped with an Apex I CCD detector and a molybdenum (Mo Kα = 0.71073 Å) sealed tube as an X-ray source. Crystals were tip-mounted on a micromount using paraffin oil. The data were processed with Oxford Diffraction Crysalis Pro software, and structure solution and refinement were performed with SHELXS and SHELXL respectively, embedded in the Olex2 package. For material composition analysis, we used XRF spectroscopy. The Amptek Complete XRF Experiment Kit was used with an Ag Mini-X tube as a source, X-123 as a detector, PX-S as an amplifier and digitizer, and XRS-FP2 quantitative analysis software to recalculate the measured XRF peak intensity into the material composition. The multiple standards calibration method was used with reference samples of known composition.

A Fluorolog iHR 320 Horiba Jobin Yvon spectrophotometer equipped with a PMT detector was used to acquire steady-state photoluminescence (PL) and PL excitation (PLE) spectra from solutions. Absolute PL quantum yield (QY) of solutions were measured with a Quantaurus-QY Absolute PL quantum yield spectrometer from Hamamatsu. 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 IDQJD-100-20-ULN avalanche photodiode (Quantique) for recording the decay traces.

**Computational Details.** Calculations were carried out at the density functional theory level as implemented in the cp2k quantum chemistry code. A doubled 2 × 2 × 2 unit cell containing 320 atoms with one Sb atom on an In position for cubic Cs₂NaInCl₆:Sb and a 1 × 1 × 2 unit cell containing 200 atoms with one Sb atom on an In position for tetragonal Cs₂KInCl₆:Sb was constructed. A mixed plane-wave and Gaussian basis set approach was used to describe the wave function and electronic density, respectively. The kinetic energy cutoff of the plane-wave basis was set to 400 Ry, while a double-ζ basis set plus polarization functions was employed to describe the molecular orbitals. The density of states (DOS) and emission and excitation energies were calculated using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional. Scalar relativistic effects have been accounted for using effective core potential functions in the basis set. Spin–orbit coupling effects were not included. Calculations with lattice relaxation for the ground state geometry optimization were performed to account for statistical disorder in the experimental crystal structures. Unit cell parameters were taken from experimental data and not relaxed, whereas atomic coordinates were optimized until the force reached 0.023 eV Å⁻¹. For the band structure calculations, the Vienna ab initio simulations package (VASP) was used. The projector augmented wave (PAW) potentials for atoms were used. For the generalized gradient approximation (GGA), the Perdew–Burke–Ernzerhof exchange–correlation functional (PBE) was used. A single cell comprising 320 atoms with a kinetic energy cutoff of 520 eV and automatic γ-centered mesh of 1 × 1 × 1 k-points were used for geometry optimization. Ionic minimization was performed until all forces on atoms were smaller than 0.001 eV Å⁻¹. A mixture of the blocked Davidson iteration scheme and the subsequent residual minimization scheme-direct inversion in the iterative subspace (RM-MDII) algorithm was used for electronic optimization. Spin–orbit coupling (SOC) was not taken into account due to the known self-interaction error that increases the valence band maximum. The band structure was calculated along a high-symmetry k-point path according to Bradley and Cracknell.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c01004.

Crystallographic data for Cs₂NaInCl₆ (CIF)

Crystal data and structure refinement for Cs₂NaInCl₆: anisotropic displacement parameters; Cs₂KInCl₆ crystal structure; XRF analysis of Sb³⁺ concentration in Cs₂NaInCl₆ and Cs₂KInCl₆: PL spectra of doped and undoped samples; PL and PLE spectra measured on powdered crystals; PLE spectra of Cs₂NaInCl₆:1% Sb at 12 K and at 300 K (PDF)

**AUTHOR INFORMATION**

Corresponding Author

Maksym V. Kovalenko — Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Bioscience, ETH Zürich, CH-8093 Zürich, Switzerland; Laboratory for Thin Films and Photovoltaics, Empa—Swiss Federal Laboratories for Materials Science and Technology, CH-8600 Dübendorf, Switzerland; orcid.org/0000-0002-6396-8938; Email: mvykovenko@ethz.ch

https://dx.doi.org/10.1021/acs.chemmater.0c01004
Chem. Mater. 2020, 32, 5118–5124

5122


Authors

Agnieszka Noculak — Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Bioscience, ETH Zurich, CH-8093 Zurich, Switzerland; Laboratory for Thin Films and Photovoltaics, Empa—Swiss Federal Laboratories for Materials Science and Technology, CH-8000 Dübendorf, Switzerland

Viktoria Morad — Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Bioscience, ETH Zurich, CH-8093 Zurich, Switzerland; Laboratory for Thin Films and Photovoltaics, Empa—Swiss Federal Laboratories for Materials Science and Technology, CH-8000 Dübendorf, Switzerland

Kyle M. McCall — Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Bioscience, ETH Zurich, CH-8093 Zurich, Switzerland; Laboratory for Thin Films and Photovoltaics, Empa—Swiss Federal Laboratories for Materials Science and Technology, CH-8000 Dübendorf, Switzerland

Sergii Yakunin — Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Bioscience, ETH Zurich, CH-8093 Zurich, Switzerland; Laboratory for Thin Films and Photovoltaics, Empa—Swiss Federal Laboratories for Materials Science and Technology, CH-8000 Dübendorf, Switzerland; 

Michael Wörle — Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Bioscience, ETH Zurich, CH-8093 Zurich, Switzerland

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.chemmatter.0c01004

Author Contributions

$A.N.$ and V.M. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the European Union through Horizon 2020 (ERC Consolidator Grant SCALE-HALO, grant agreement no. [819740]) and by ETH Zurich (ETH + Project SynMatLab). A.N. acknowledges partial financial support from the EMPAPOSTDOCS-II program, which received funding from the European Union’s Horizon 2020 Research and Innovation Program under the Marie Skłodowska-Curie grant agreement number 754364. The authors would like to acknowledge Kostiantyn Sakhatskyi for the X-ray fluorescence measurements, as well as Bogdan Benin and Dr Simon Boehme for fruitful discussions.

REFERENCES

(1) Yoon, H. C.; Lee, H.; Kang, H.; Oh, J. H.; Do, Y. R. Highly Efficient Wide-Color-Gamut QD-Emissive LCDs Using Red and Green Perovskite Core/Shell QDs. J. Mater. Chem. C 2018, 6, 13023–13033.

(2) Ko, Y. H.; Jalalah, M.; Lee, S. J.; Park, J. G. Super Ultra-High Resolution Liquid-Crystal-Display Using Perovskite Quantum-Dot Functional Color Filters. Sci. Rep. 2018, 8, No. 12881.

(3) Chiba, T.; Hayashi, Y.; Ebe, H.; Hoshi, K.; Sato, J.; Sato, S.; Pu, Y. J.; Ohisa, S.; Kido, J. Anion-Exchange Red Perovskite Quantum Dots with Ammonium Iodine Salts for Highly Efficient Light-Emitting Devices. Nat. Photonics 2018, 12, 681–687.

(4) Lin, K. B.; Xing, J.; Quan, L. N.; de Arquer, F. P. G.; Gong, X. W.; Lu, J. X.; Xie, L. Q.; Zhao, W. J.; Zhang, D.; Yan, C. Z.; Li, W. Q.; Liu, X. Y.; Lu, Y.; Kirman, J.; Sargent, E. H.; Xiong, Q. H.; Wei, Z. H. Perovskite Light-Emitting Diodes with External Quantum Efficiency Exceeding 20%. Nature 2018, 562, 245–248.

(5) Yakunin, S.; Protessescu, L.; Krieg, F.; Bodnarchuk, M. I.; Nedelcu, G.; Humer, M.; De Luca, G.; Fiebig, M.; Heiss, W.; Kovalenko, M. V. Low-Threshold Amplified Spontaneous Emission and Lasing from Colloidal Nanocrystals of Caesium Lead Halide Perovskites. Nat. Commun. 2015, 6, No. 8056.

(6) Tan, Z. K.; Moghaddam, R. S.; Lai, M. M.; Docampo, P.; Higler, R.; Deschler, F.; Price, M.; Sbadhana, A.; Pazos, L. M.; Credgington, D.; Hanusch, F.; Bein, T.; Snait, H. J.; Friend, R. H. Bright Light-Emitting Diodes Based on Organometal Halide Perovskite. Nat. Nanotechnol. 2014, 9, 687–692.

(7) Brenner, P.; Bar-On, O.; Jakoby, M.; Allegro, I.; Richards, B. S.; Paetzold, U. W.; Howard, I. A.; Scheuer, J.; Lemmer, U. Continuous Wave Amplified Spontaneous Emission in Phase-Stable Lead Halide Perovskites. Nat. Commun. 2019, 10, No. 988.

(8) Zhu, H. M.; Fu, Y. P.; Meng, F.; Wu, X. X.; Gong, Z. Z.; Ding, Q.; Gustafsson, M. V.; Trinh, M. T.; Jin, S.; Zhu, X. Y. Lead Halide Perovskite Nanowire Lasers with Low Lasing Thresholds and High Quality Factors. Nat. Mater. 2015, 14, 636–642.

(9) Utrat, H.; Sun, W. W.; Kaplan, A. E. K.; Krieg, F.; Ginterseder, M.; Spokoyny, B.; Klein, N. D.; Shulenberg, K. E.; Perkinsson, C. F.; Kovalenko, M. V.; Bawendi, M. G. Coherent Single-Photon Emission from Colloidal Lead Halide Perovskite Quantum Dots. Science 2019, 363, 1068–1072.

(10) Luo, J. J.; Wang, X. M.; Li, S. R.; Liu, J.; Guo, Y. M.; Niu, G. D.; Yao, L.; Fu, Y. H.; Gao, L.; Dong, Q. S.; Zhao, C. Y.; Leng, M. Y.; Ma, F. S.; Liang, W. X.; Wang, L. D.; Jin, S. Y.; Han, J. B.; Zhang, L. J.; Etheridge, J.; Wang, J. B.; Yan, Y. F.; Sargent, E. H.; Tang, J. Efficient and Stable Emission of Warm-White Light from Lead-Free Halide Double Perovskites. Nature 2018, 563, 541–545.

(11) Chen, Q. S.; Wu, J.; Ou, X. Y.; Huang, B. L.; Almutlaq, J.; Zhumenkov, A. A.; Guan, X. W.; Han, S. Y.; Liang, L. Y.; Yi, Z. G.; Li; Jie; Xie, X. J.; Wang, Y.; Li, Y.; Fan, D. Y.; Teh, D. B. L.; All, A. H.; Mohammed, O. F.; Bakr, O. M.; Wu, T.; Bettinelli, M.; Yang, H. H.; Huang, W.; Liu, X. G. All-Inorganic Perovskite Nanocrystal Scintillators. Nature 2018, 561, 88–93.

(12) Yakunin, S.; Benin, B. M.; Shynkarenko, Y.; Nazareno, O.; Bodnarchuk, M. I.; Dirin, D. N.; Hofer, C.; Cattaneo, S.; Kovalenko, M. V. High-Resolution Remote Thermometry and Thermography Using Luminescence Low-Dimensional Tin-Halide Perovskites. Nat. Mater. 2019, 18, 846–852.

(13) Meinardi, F.; Akkerman, Q. A.; Bruni, F.; Park, S.; Mauri, M.; Dang, Z. Y.; Manna, L.; Brovelli, S. Doped Halide Perovskite Nanocrystals for Reabsorption-Free Luminescent Solar Concentrators. ACS Energy Lett. 2017, 2, 2368–2377.

(14) Milstein, T. J.; Kroupa, D. M.; Gamelin, D. R. Picosecond Quantum Cutting Generates Photoluminescence Quantum Yields Over 100% in Ytterbium-Doped CsPbCl3 Nanocrystals. Nano Lett. 2018, 18, 3792–3799.

(15) Pazos-Outon, L. M.; Szumulo, M.; Lamboll, R.; Richter, J. M.; Crespo-Quésada, M.; Abdi-Jalebi, M.; Besson, H. J.; Vrucinic, M.; Alsari, M.; Snaith, H. J.; Etherer, B.; Friend, R. H.; Deschler, F. Photon Recycling in Lead Iodide Perovskite Solar Cells. Science 2016, 351, 1430–1433.

(16) Hayes, R. L. Z.; Eyre, L.; Wei, F. X.; Brivio, F.; Sbadhana, A.; Sun, S. J.; Li, W. W.; Zhang, K. H. L.; MacManus-Driscoll, J. L.; Bristowe, P. D.; Friend, R. H.; Cheetham, A. K.; Deschler, F. Fundamental Carrier Lifetime Exceeding 1 μs in Cs₅AgBr₆ Double Perovskite. Adv. Mater. Interfaces 2018, 5, No. 1800464.

(17) Kovalenko, M. V.; Protessescu, L.; Bodnarchuk, M. I. Properties and Potential Optoelectronic Applications of Lead Halide Perovskite Nanocrystals. Science 2017, 358, 745–750.
(18) Smith, M. D.; Connor, B. A.; Karunadasa, H. I. Tuning the Luminescence of Layered Halide Perovskites. *Chem. Rev.* **2019**, *119*, 3104–3139.

(19) Mao, L. L.; Guo, P. J.; Kepenekian, M.; Hadar, I.; Katan, C.; Even, J.; Schaller, R. D.; Stompos, C. C.; Kanatzidis, M. G. Structural Diversity in White-Light-Emitting Hybrid Lead Bromide Perovskites. *J. Am. Chem. Soc.* **2018**, *140*, 13078–13088.

(20) Romanov, A. N.; Haula, E. V.; Kouznetsov, M. S.; Liatsksy, I. S.; Pimkin, N. A.; Boldyrev, K. N.; Sereda, A. E.; Shashkin, D. P.; Korchak, V. N. Preparation of Optical Media with NIR Luminescent Bi⁺ Impurity Centers by Ion Exchange. *J. Am. Ceram. Soc.* **2019**, *102*, 2745–2751.

(21) Vandersteen, A. C.; Dirksen, G. J. Luminescence and Crystal-Growth of Cs₂NaYCl₆. *Chem. Phys. Lett.* **1978**, *59*, 110–112.

(22) Nikl, M.; Mihokova, E.; Nitsch, K. Photoluminescence and Decay Kinetics of CsPbCl₃ Single-Crystals. *Solid State Commun.* **1992**, *84*, 1089–1092.

(23) Morad, V.; Shynkarenko, Y.; Yakunin, S.; Brumberg, A.; Schaller, R. D.; Kovalenko, M. V. Disphenoidal Zero-Dimensional Lead, Tin, and Germanium Halides: Highly Emissive Singlet and Triplet Self-Trapped Excitons and X-ray Scintillation. *J. Am. Chem. Soc.* **2019**, *141*, 9764–9768.

(24) Zhou, C. K.; Worku, M.; Neu, J.; Lin, H. B.; Tian, Y.; Lee, S. J.; Zhou, Y.; Han, D.; Chen, S. Y.; Hao, A.; Djurovich, P. L.; Siegert, T.; Du, M. H.; Ma, B. W. Facile Preparation of Light Emitting Organic Metal Halide Crystals with Near-Unity Quantum Efficiency. *Chem. Mater.* **2018**, *30*, 2374–2378.

(25) Li, Z. Y.; Li, Y.; Liang, P.; Zhou, T. L.; Wang, L.; Xie, R. J. Dual-Band Luminescent Lead-Free Antimony Chloride Halides with Near-Unity Photoluminescence Quantum Efficiency. *Chem. Mater.* **2019**, *31*, 9363–9371.

(26) Sedakov, T. V.; Mirochnik, A. G.; Karasev, V. E. Structure and Luminescence Properties of Antimony(III) Complex Compounds. *Opt. Spectrosc.* **2008**, *105*, 517–523.

(27) Zhou, C. K.; Lin, H. B.; Tian, Y.; Yuan, Z.; Clark, R.; Chen, B. H.; van de Burgt, L.; Wang, J. C.; Zhou, Y.; Hanson, K. J.; Meisner, Q. J.; Neu, J.; Besara, T.; Siegert, T.; Lambers, E.; Djurovich, P.; Ma, B. W. Luminescent Zero-Dimensional Organic Metal Halide Hybrids with Near-Unity Quantum Efficiency. *Chem. Sci.* **2018**, *9*, 586–593.

(28) McCall, K. M.; Friedrich, D.; Chica, D. G.; Cai, W. Z.; Stompos, C. C.; Alexander, G. C. B.; Deeyam, S.; Wessels, B. W.; Kanatzidis, M. G. Perovskites with a Twist: Strong In¹+ Off-Centering in the Mixed-Valent CsInX₃ (X = Cl, Br). *Chem. Mater.* **2019**, *31*, 9554–9566.

(29) Oomen, E. W. J. L.; Smit, W. M. A.; Blasse, G. The Luminescence of Cs₂NaSnCl₆ and Cs₂NaSnBr₆ - a Transition from a Localized to a Delocalized Excited-State. *Chem. Phys. Lett.* **1987**, *138*, 23–28.

(30) Jacobs, P. W. M. Alkali-Halide Crystals Containing Impurity Ions with the ns² Ground-State Electronic Configuration. *J. Phys. Chem. Solids* **1991**, *52*, 35–67.

(31) Jing, Y. Y.; Liu, Y.; Zhao, J.; Xia, Z. G. Sn³⁺ Doping-Induced Triplet Self-Trapped Excitons Emission in Lead-Free Cs₂SnCl₄ Nanocrystals. *J. Phys. Chem. Lett.* **2019**, *10*, 7439–7444.

(32) Volonaksis, G.; Filip, M. R.; Haghighirad, A. A.; Sakai, N.; Wenger, B.; Snath, H. J.; Giustino, F. Lead-Free Halide Double Perovskites via Heterovalent Substitution of Noble Metals. *J. Phys. Chem. Lett.* **2016**, *7*, 1254–1259.

(33) Meng, W. W.; Wang, X. M.; Xiao, Z. W.; Wang, J. B.; Mitra, D. B.; Yan, Y. F. Parity-Forbidden Transitions and Their Impact on the Optical Absorption Properties of Lead-Free Metal Halide Perovskites and Double Perovskites. *J. Phys. Chem. Lett.* **2017**, *8*, 2999–3007.

(34) Oomen, E. W. J. L.; Dirksen, G. J. Crystal-Growth and Luminescence of Sb³⁺-Doped Cs₂NaScCl₆, Cs₂NaYCl₆, Cs₂NaLaCl₆, Cs₂NaBr₆, and Cs₂NaIₖ. *Mater. Res. Bull.* **1985**, *20*, 453–457.

(35) Oomen, E. W. J. L.; Dirksen, G. J.; Smit, W. M. A.; Blasse, G. On the Luminescence of the Sb³⁺ Ion in Cs₂NaScCl₆, Cs₂NaYBr₆, Cs₂NaLaBr₆. *J. Phys. C: Solid State Phys.* **1987**, *20*, 1161–1171.