Zwitterions in 3D Perovskites: Organosulfide-Halide Perovskites

Jiayi Li, Zhihengyu Chen, Santanu Saha, James K. Utterback, Michael L. Aubrey, Rongfeng Yuan, Hannah L. Weaver, Naomi S. Ginsberg, Karena W. Chapman, Marina R. Filip,* and Hemamala I. Karunadasa*

ABSTRACT: Although sulfide perovskites usually require high-temperature syntheses, we demonstrate that organosulfides can be used in the milder syntheses of halide perovskites. The zwitterionic organosulfide, cysteamine (CYS; \( \text{NH}_2(\text{CH}_2)_2\text{S}^- \)), serves as both the \( X^- \) site and \( A^+ \) site in the ABX\(_3\) halide perovskites, yielding the first examples of 3D organosulfide-halide perovskites: \((\text{CYS})\text{PbX}_2\) (\( X^- = \text{Cl}^- \) or \( \text{Br}^- \)). Notably, the band structures of \((\text{CYS})\text{PbX}_2\) capture the direct bandgaps and dispersive bands of \( \text{APbX}_3 \) perovskites. The sulfur orbitals compose the top of the valence band in \((\text{CYS})\text{PbX}_2\), affording unusually small direct bandgaps of 2.31 and 2.16 eV for \( X^- = \text{Cl}^- \) and \( \text{Br}^- \), respectively, falling in the ideal range for the top absorber in a perovskite-based tandem solar cell. Measurements of the carrier dynamics in \((\text{CYS})\text{PbCl}_2\) suggest carrier trapping due to defects or lattice distortions. The highly desirable bandgaps, band dispersion, and improved stability of the organosulfide perovskites demonstrated here motivate the continued expansion and exploration of this new family of materials, particularly with respect to extracting photocurrent. Our strategy of combining the \( A^+ \) and \( X^- \) sites with zwitterions may offer more members in this family of mixed-anion 3D hybrid perovskites.

HALIDE perovskites have risen as contenders for low-cost and efficient solar-cell absorbers.\(^1,2\) However, the composition that can deliver the desired efficiency and stability remains to be found.\(^3\) In particular, a perovskite with a \( \sim 2 \) eV bandgap is highly sought for the top absorber in a high-efficiency dual-\(^1\) or triple-junction \(^1\) tandem solar cell.\(^6\) Although bromide-rich \( \text{APb(Br,I)}\(_x\)\(\text{I}_y\)\) perovskites display such bandgaps, light-induced halide segregation precludes high voltages from being realized with these perovskites.\(^7\) We therefore sought a different type of anion mixing to expand the accessible bandgaps of lead-halide perovskites. Herein, we report a new family of 3D halide perovskites, where a zwitterionic organosulfide serves as both the cationic \( A^+ \) site and an anionic \( X^- \) site in the \( \text{APb}^\text{L}\text{X}_3 \) (\( X^- = \text{halide} \)) formula, yielding the general formula \( \text{LPb}^\text{L}\text{X}_2 \) (here, \( L = \text{CYS} = \text{NH}_2(\text{CH}_2)_2\text{S}^- \) and \( X^- = \text{Cl}^- \) or \( \text{Br}^- \)). Notably, the calculated electronic structures of \((\text{CYS})\text{PbX}_2\) show direct bandgaps and dispersive frontier bands—capturing the highly desirable characteristics of the \( \text{APbX}_3 \) perovskites. Further, the dominant \( S \) contribution to the valence band reduces the bandgaps of \((\text{CYS})\text{PbX}_2\) (2.31 and 2.16 eV for \( X^- = \text{Cl}^- \) and \( \text{Br}^- \), respectively) compared to those of the \((\text{MA})\text{PbX}_2\) perovskites (2.98 and 2.24 eV for \( X^- = \text{Cl}^- \) and \( \text{Br}^- \), respectively). The substitution of heavier halides affords smaller bandgaps in perovskites, but at the cost of stability. In contrast, replacement of \( \text{Cl}^- \) or \( \text{Br}^- \) with \( \text{S}^- \) reduces the perovskite’s bandgap and enhances stability to moderate heat and high humidity.

Expanding the compositional diversity of halide perovskite solar absorbers is key for improving upon their drawbacks.\(^8\) The direct bandgap of lead-halide perovskites is determined by the halide and lead frontier orbitals.\(^9\) Thus, halide mixing is a common strategy for modulating the bandgap, explored since the 1970s.\(^10,11\) However, halide mobility\(^12\) and light-induced halide segregation\(^1\) impede stable optoelectronic properties from being realized in numerous mixed-halide compositions.

Anions such as \( \text{S}^2^- \), \( \text{H}^+ \), \( \text{N}^3^- \), \( \text{Cl}^- \) have been substituted for the oxides in oxide perovskites\(^13\)–\(^16\). In contrast, anion mixing in halide perovskites is limited to halides, and in 2D perovskites, to halides and pseudohalides (\( \text{SCN}^- \), \( \text{I}^- \)).\(^11\) Inspired by mixed-anion oxide perovskites, we sought to incorporate chalcogenides into halide perovskites. Sulfide perovskites such as \( \text{BaZrS}_3 \) and \( \text{SrZrS}_3 \) show bandgaps suitable for photovoltaic applications, and have greater heat and moisture stability compared to the halides.\(^17\) However, sulfide perovskites are synthesized at high temperatures (800–1000 °C), and the study of their charge transport is in the early stages.\(^18\) An obvious obstacle to introducing \( \text{S}^2^- \) into halide perovskites is charge balance. We therefore considered organosulfides (\( \text{RS}^- \)) as more suitable ligands to replace halides. To accommodate the larger organosulfides into a 3D perovskite, we combined the \( A^+ \) site and the \( X^- \) site—essentially replacing \( \text{CH}_3\text{NH}_3^+ \) and \( X^- \) with \( \text{RS}^- \) (Figure 1). We recently discovered that zwitterionic cysteamine (\( \text{CYS} \)) can template intergrowths in 2D perovskites to afford layered heterostructures.\(^19\) The related disulfide (\( \text{H}_2\text{N}(\text{CH}_2)_2\text{S}^-\text{S}^- (\text{CH}_2)_2\text{NH}_4^+ \))\(^20\) and thiol (\( \text{H}_2\text{N}(\text{CH}_2)_2\text{SH} \))\(^21\) form 2D lead-halide perovskite intergrowths.
halide perovskites. However, CYS has promising features for incorporation into a 3D perovskite: (1) the ammonium head in CYS may serve as the A site; (2) CYS is known to form Pb–S bonds; and (3) the similarly sized ethylammonium has been incorporated into 3D perovskites, albeit in substoichiometric amounts.

Combining equal amounts of PbX₂ (X’ = Cl⁻, Br⁻) and CYS in dimethylformamide at 150 °C under N₂ affords a yellow or red solid, respectively, which was filtered while hot. Elemental analysis of the materials is consistent with the formula (CYS)PbX₂. Note that lower temperatures yield the perovskite heterostructure instead. This method affords phase-pure (CYS)PbCl₂, although the synthesis of (CYS)-PbBr₂ contains ca. 5% of the heterostructure impurity. A mixture of CYS and CYS-HCl slows the crystallization to afford single crystals of (CYS)PbCl₂ (Figure S1). Single-crystal X-ray diffraction revealed the structure as a 3D perovskite in the R̅3c space group, with a heavily disordered organic component and indistinguishable Cl/S sites. Based on the formula, we expect each lead to be coordinated by 4 halides within the typical energy range for metal sulfides (Figure S6), whereas thiols (RSH) have a higher binding energy of 164 eV.

Figure 2. Room-temperature structures of (A) (CYS)PbCl₂ and (B) (CYS)PbBr₂ derived from pair distribution function (PDF) analysis with the disordered organoammonium tail of CYS represented by a gray sphere. Turquoise, green, brown, gray spheres represent Pb, Cl/ S, Br/S, and K (proxy) atoms, respectively. (C) PDF analysis of (CYS)PbCl₂ and (CYS)PbBr₂.

Diffuse reflectance spectra of (CYS)PbX₂ powders show strong absorption onsets, with optical gaps of 2.31 and 2.16 eV for (CYS)PbCl₂ and (CYS)PbBr₂ (Figure 2C), respectively.
calculated using direct-bandgap Tauc plots (Figure S12). The difference between the experimental bandgaps for (CYS)PbCl$_2$ and (CYS)PbBr$_2$ (0.15 eV) agrees with our DFT calculations (0.15 eV). The bandgap of (CYS)PbCl$_2$ is smaller than that of orthorhombic (MA)PbCl$_3$ by ca. 0.7 eV, and the difference in bandgaps between chlorides and bromides is much smaller for (CYS)PbX$_2$ (0.15 eV) than for (MA)PbX$_3$ (0.74 eV). These features are consistent with the lesser electronegativity of S compared to Cl and the smaller halide contribution (<10%) in the VBM of (CYS)PbX$_2$.

Although (MA)PbX$_3$ exhibits narrow, band-edge photoluminescence (PL) at room temperature (Figure S13), (CYS)PbX$_2$ shows broad PL only at low temperature (80 K; Figure 5A) with a large Stokes shift, suggesting strong electron–phonon interactions or the presence of defects. Similar broad PL from 2D Pb–X (X = Cl, Br) perovskites are attributed to exciton–phonon (self-trapping) interactions.

We further probed the carrier dynamics in (CYS)PbCl$_2$ single crystals. The weak room-temperature PL, measured by time-correlated single photon counting (TCSPC), exhibits an instrument response-limited component followed by a 0.9 ns decay (Figure 5B), which is similar to the PL lifetime of a (MA)PbCl$_3$ crystal (1.6 ns). Some variation in the PL
lifetime of different crystals (0.9−3.1 ns) is consistent with a defect-mediated emission.

We then applied stroboscopic scattering microscopy (stroboSCAT) to directly measure the microscopic carrier behavior.33−35 We excited a (CYS)PbCl₃ crystal with a 470 nm light pulse (~100 ps pulse) focused to a 278 nm spot size (full width at half maximum). The resulting excited carrier profile was imaged using a time-delayed widefield 635 nm probe light pulse. The image contrast is proportional to the carrier-induced changes to the material’s refractive index.33,34 Comparing images at different pump−probe time delays to dark reference images gives the spatiotemporal transient reflectance images, ΔR/R (Figure S14). We fit the radial expansion of the carrier distribution to a Gaussian profile of width σ over time t to find the mean-squared expansion, σ²(t) − σ²(0). The mean-squared expansion is nonlinear, transitioning from a relatively high diffusivity (Dfast), which persists over 100 ps−1 ns, to a lower diffusivity (Dslow) that persists to at least 100 ns (Figure S15). Fitting the mean-squared expansion to 2DΔt for t = 100 ps to 1 ns (Figure S5C), where carriers persist in the emissive state measured by TCSPC, gives Dfast = 3.1(2) × 10⁻⁷ cm²/s. This value can be related to the mobility (μ) through the Einstein relation, eD = μkB₅ where e is the elementary charge, k₅ is the Boltzmann constant, and T is the temperature—to give μ = 1.4 cm²/V-s. The lower mobility in (CYS)PbCl₃ compared to that of a (MA)PbCl₃ single crystal (42 cm²/V-s)37 could be due to surface defects or enhanced carrier/exciton−phonon coupling in (CYS)PbCl₃, as seen in other chloride perovskites.

The (CYS)PbX₃ perovskites exhibit higher stability toward moisture and extended mild heating compared to (MA)PbX₃, which may be due to the Pb−S covalency. The PXRD patterns of (CYS)PbX₃ after moisture exposure (100% RH, 10 days for X⁻ = Cl⁻ and 5 days for X⁻ = Br⁻) or heating (60 °C in air, 30 days for X⁻ = Cl⁻ and 15 days for X⁻ = Br⁻) showed no evidence of decomposition (Figure S18). In contrast, (MA)PbX₃ showed decomposition after exposure to the 100% RH (1 day for X⁻ = Cl⁻ and Br⁻) or heating at 60 °C (10 days for X⁻ = Cl⁻ and 8 days for X⁻ = Br⁻). Thermal stability at higher temperatures is discussed in the Supporting Information.

Organosulfides allow sulfur to be incorporated into lead-halide perovskites at mild temperatures, circumventing the formation of PbS. The new LPbX₃ perovskites (L = zwiterton) largely preserve the desirable electronic band structure of the APbX₃ perovskites. Incorporating heavier halides and chalcogenides into LPbX₃ and passivating defects may improve carrier mobility for charge extraction. Overall, (CYS)PbX₃ combines characteristics of PbS and APbX₃—two important families of solar absorbers—and we expect that these are the first members of a larger family of organochalcogenide-halide perovskites.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c09382.

Experimental and computational details, crystallographic data, and spectra (PDF)

Additional DFT and PDF CIF files (ZIP)

**Accession Codes**

CCDC 2205034 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

### AUTHOR INFORMATION

**Corresponding Authors**

Marina R. Filip — Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0003-2925-172X; Email: marina.filip@physics.ox.ac.uk

Hemamala I. Karunadasa — Department of Chemistry, Stanford University, Stanford, California 94305, United States; Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States; orcid.org/0000-0003-4949-8068; Email: hemamala@stanford.edu

**Authors**

Jiayi Li — Department of Chemistry, Stanford University, Stanford, California 94305, United States
Zhihengyu Chen — Department of Chemistry, Stony Brook University, Stony Brook, New York 11794, United States; orcid.org/0000-0001-5882-7076
Santanu Saha — Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom
James K. Utterback — Department of Chemistry, University of California, Berkeley, California 94720, United States; orcid.org/0000-0002-9296-841X
Michael L. Aubrey — Department of Chemistry, Stanford University, Stanford, California 94305, United States; Present Address: M.L.A.: Department of Chemistry, University of Texas at Austin, Texas, 78712, United States; orcid.org/0000-0002-0740-0731
Rongfeng Yuan — Department of Chemistry, University of California, Berkeley, California 94720, United States; orcid.org/0000-0002-6572-2472
Hannah L. Weaver — Department of Chemistry, University of California, Berkeley, California 94720, United States
Naomi S. Ginsberg — Department of Chemistry, University of California, Berkeley, California 94720, United States; STROBE, National Science Foundation Science and Technology Center and Department of Physics, University of California Berkeley, Berkeley, California 94720, United States; Materials Science Division and Molecular Biophysics and Integrated Bioimaging Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States; Kavli Energy NanoSciences Institute at Berkeley, Berkeley, California 94720, United States; orcid.org/0000-0002-5660-3586
Karen W. Chapman — Department of Chemistry, Stony Brook University, Stony Brook, New York 11794, United States; orcid.org/0000-0002-8725-5633

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/jacs.2c09382

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the Brown Science Foundation. J.L. acknowledges a Stanford Interdisciplinary Graduate Fellowship and M.L.A. acknowledges an Office of Energy
Efficiency and Renewable Energy (EERE) postdoctoral fellowship. M.R.F. acknowledges support of the John Fell Oxford University Press (OUP) Research Fund. S.S. and M.R.F. acknowledge support from the UK Engineering and Physical Sciences Research Council (EPSRC), Grant EP/V010840/1. S.S. and M.R.F. accessed computational resources accessed via our membership of the UK’s HEC Materials Chemistry Consortium, which is funded by EPSRC (EP/R029431). SCXRD studies were performed at the Stanford Nano Shared Facilities (SNSF), supported by the National Science Foundation (NSF) under award ECCS-1542152. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under contract no. DE-AC02-06CH11357. The stroboSCAT measurements and analysis were supported by STROBE, a NSF Science & Technology Center under Grant No. DMR 1548924. J.K.U. acknowledges support from the Camille and Henry Dreyfus Foundation’s Postdoctoral Program in Environmental Chemistry. N.S.G. acknowledges a David and Lucile Packard Foundation Fellowship for Science and Engineering and a Camille and Henry Dreyfus Teacher-Scholar Award.

REFERENCES


**NOTE ADDED AFTER ASAP PUBLICATION**

This paper was published ASAP on November 23, 2022. CIF files that were not available with the original ASAP publication have been added to the Supporting Information. The corrected version was reposted on November 29, 2022.