PERSPECTIVE

# Halide Perovskites under Pressure: Accessing New Properties through Lattice Compression

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ABSTRACT: Lattice compression allows for systematic structural tuning without changing composition. Halide perovskites are a large and diverse family of solids, which have enormous potential for applications in energy capture, storage, and utilization. Notably, they have soft lattices and their photophysical and transport properties exhibit a large pressure response. In this Perspective, we highlight how pressure can alter their electronic landscapes, affect excited-state dynamics, and afford new structures not accessible through conventional syntheses. We further discuss how the insight we gain from high-pressure studies expands the scope of these versatile materials in current and future energy applications.
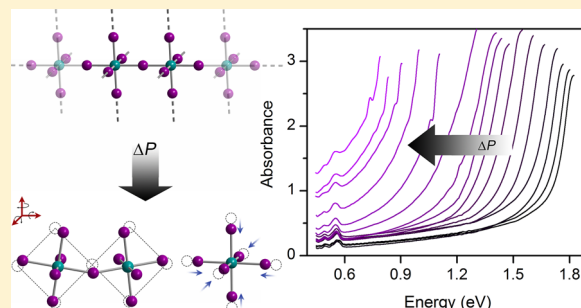
Halide perovskites exhibit remarkable optical and electronic diversity, enabling their implementation in technologies such as photovoltaics, artificial illumination, and electrochemical energy storage.[1] For example, the strong band-edge absorption and long carrier lifetimes of 3D perovskites afford efficient photocurrent generation in solar cells,[2] whereas the excitonic emission from 2D perovskites has been used in various luminescent devices.[1] For their structural diversity to be fully leveraged for targeted properties, a clear understanding of the relationship between their physical structures and electronic properties is required. Several studies have investigated this relationship in as-synthesized perovskites[1] and in perovskites accessed through postsynthetic reactions.[3] Here, we examine how lattice compression systematically modulates the structures and the electronic landscapes of these compressible solids and induces new photophysical and transport properties. Pressure is a powerful tool for

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accessing new thermodynamic properties while also affecting excited-state dynamics. By providing systematic control over interatomic distance, a primary input for calculations of solid-state properties, high-pressure studies also provide experimental support for theoretical models.[4]

High-Pressure Studies. Static compression, achieved through the development of the diamond-anvil cell (DAC), has enabled studies up to hundreds of GPa (1 GPa ≈ 10 000 atm).[5] A DAC typically consists of a pair of gem-quality single-crystal diamond tips, which are used to compress a sample immersed in a pressure-transmitting medium such as helium. Liquid helium solidifies at 11 GPa,[5] the highest solidification pressure among all fluids, and provides good quasi-hydrostatic conditions up to 100 GPa. The excellent transparency of diamonds to a wide range of electromagnetic radiation allows for a suite of optical and synchrotron X-ray probes to be coupled with DACs. High-pressure transport measurements within DACs, such as electrical conductivity and magnetic susceptibility, have also been developed.[5] With these advances in high-pressure characterization, it is an opportune time to explore the effects of pressure on the properties of technologically important materials.

Halide Perovskites: Structure. Halide perovskites consist of corner-sharing B—X octahedra (B = metal, X = halide) that form frameworks in 0, 1, 2, or 3 dimensions. To compensate for the charge of the anionic inorganic frameworks, these lattices incorporate inorganic or organic cations. Small cations occupy the A-site cavities of 3D perovskites (of the form ABX_3; Figure 1A), whereas larger A-site cations separate the inorganic sheets of 2D perovskites (of the form A_2BX_4; Figure 1B). Perovskite structures are typically limited by the steric and electronic interactions that dictate crystal packing and metal—ligand interactions. Mechanical compression provides the means to overcome these limitations and access wider structural diversity without changing composition. Applied pressure can induce
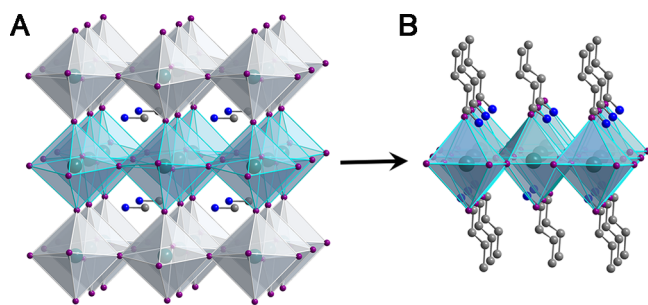
Figure 1. Single-crystal X-ray structures of (A) 3D (MA)PbI$_3$ (MA = CH$_3$NH$_3{}^+$) and (B) 2D (C$_4$H$_9$NH$_3$)$_2$PbI$_4$. The 2D perovskite can be structurally derived from the 3D perovskite by slicing along the (001) crystallographic plane (turquoise octahedra). Turquoise, purple, gray, and blue spheres represent Pb, I, C, and N atoms, respectively. H and disordered atoms were omitted for clarity.

changes to the metal coordination sphere (bond lengths or octahedral regularity) and interoctahedral tilting, as well as interlayer spacing in 2D perovskites. Compression can also modulate the perovskite's dielectric landscape by altering both material density and lattice packing arrangements.

Halide Perovskites: Electronic Properties. Halide perovskites have bandgaps ranging from ~1 to 3 eV. Their bandgap edges have mostly metal and halide character.[6] For example, lead halide perovskites have predominantly halide p and metal s orbital character at the valence band maximum, while vacant metal p orbitals dominate the conduction band minimum.[6] Similarly, the dominant electronic transition in copper halide perovskites is charge transfer from halide p orbitals to Cu d orbitals.[7] Therefore, compositional and structural changes to the B−X lattice significantly affect their photophysical and transport properties. The A-site cations also exert an indirect, but important, effect on the electronic structure by inducing distortions in the inorganic framework through templating effects[1] as well as by modulating the material's dielectric constant.[8] The effects of compression have been examined for perovskites whose electronic structures range from almost molecular in nature (e.g., 2D Cu−Cl perovskites),[9−11] to medium-bandgap semiconductors (e.g., 3D Pb−I perovskites),[12−17] to doped semiconductors with metallic transport properties[18] (e.g., 3D Sn−I perovskites).[19,20]

Bulk Moduli. The bulk modulus at ambient pressure (K_0) measures a lattice's susceptibility to compression. Hybrid halide perovskites for which typically $K_0 < 20$ GPa[10,11,13,20−22] are far softer than oxide perovskites that usually have $K_0 > 100$ GPa.[23] Within hybrid halide perovskites, there appear to be clear distinctions in bulk moduli for 2D and 3D analogues. The reported K_0 values of 3D hybrid perovskites fall in a narrow range of 12−18 GPa.[13,20,21] Here, different organic and inorganic components play a minimal role in determining material compressibility. In contrast, 2D hybrid perovskites exhibit a larger range of K_0 values from 7 to 22 GPa.[10,11,22] The 2D (MA)$_2$PbI$_2$(SCN)$_2$ even shows bulk elastic properties of similar softness to molecular solids,[22] indicating that low levels of compression/strain can strongly tune these structures.

Structural Effects of Compression. Compression induces a variety of structural changes in halide perovskites including symmetry-altering phase transitions, local distortions in the inorganic lattice, and partial amorphization.[10−17,19−22,24] Importantly, a high degree of crystallinity is maintained within many of their high-pressure phases, allowing for characterization through standard diffraction techniques.

Distortions in the Inorganic Lattice. Upon compression, the inorganic lattice relaxes through two main avenues: octahedral tilting and bond contraction (Figure 2). While both effects can
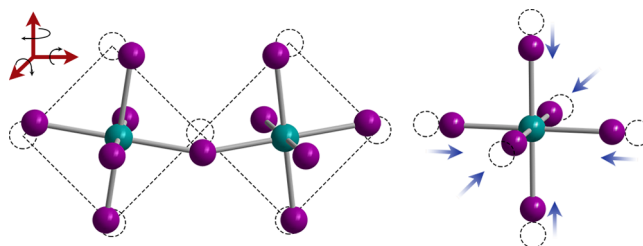

Figure 2. Structural effects of compression on the inorganic lattice in metal halide perovskites: octahedral tilting (left) and bond compression (right). Turquoise and purple spheres represent metals and halides, respectively. Dashed lines indicate original atom positions.

occur at lower pressures (<5 GPa), octahedral tilting tends to dominate in this pressure range. At relatively low pressures, (MA)PbX$_3$ (X = Br$^-$, I$^-$), which have recently emerged as high-efficiency photovoltaic absorbers, undergo first-order phase transitions to a cubic β phase with the space group $Im\bar{3}$,[13,14,16,24] although some reports claim alternate space groups.[15,17] These transitions are accompanied by severe deviation of the Pb−X−Pb angles from 180°, which can be visualized as rotations of metal halide octahedra about the Cartesian axes (Figure 2).[25] At ~0.3 GPa, (MA)PbI$_3$ transitions from the low-pressure α phase to the high-pressure β phase through such octahedral tilting (Figure 3). At higher pressures, significant metal halide bond contraction occurs in addition to further octahedral tilting.
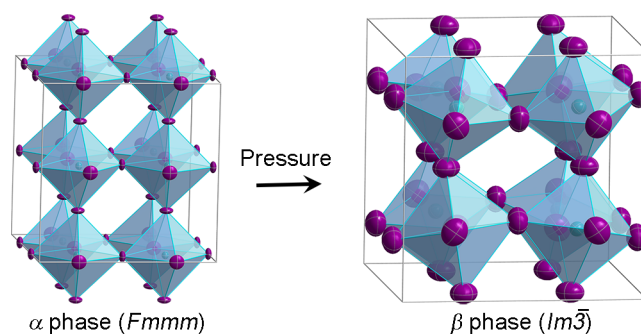

Figure 3. Single-crystal X-ray structures of (MA)PbI$_3$ at ambient pressure (α phase) and 0.7 GPa (β phase). Turquoise and purple ellipsoids represent Pb and I atoms, respectively. Disordered atoms and MA cations were omitted for clarity. Adapted from ref 13.

Octahedral tilting and metal halide bond contraction also occur during compression of 2D Cu−Cl perovskites.[9−11] The high-pressure properties of these perovskites have been extensively studied, in part due to their structural similarities to the cuprate superconductors, whose critical temperatures (T_c) show a pressure dependence.[26] A half-filled band should provide a conduction pathway, but poor orbital overlap promoted by the pronounced Jahn−Teller (JT) distortion of the 3d^9 Cu^{II} centers leads to these materials' insulating behavior and translucent yellow color. Here, the antiferrodistortive alignment of the elongated axes in the Cu−Cl octahedra, which lie in the plane of the inorganic layers (Figure 4B), results in
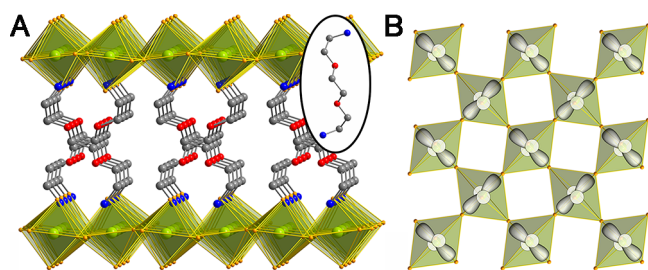
Figure 4. (A) Single-crystal X-ray structure of (EDBE)CuCl$_4$. (Inset) EDBE dication. Green, orange, gray, blue, and red spheres represent Cu, Cl, C, N, and O, respectively. H atoms were omitted for clarity. (B) Cu−Cl layer with schematic d$_{x^2-y^2}$ orbitals overlaid to illustrate their orthogonality. Adapted from ref 11.

orthogonal half-filled d$_{x^2-y^2}$ orbitals. The question of whether mechanical compression can overcome the electronic stabilization provided by the JT distortion has been substantially debated in the literature. Early reports attributed a first-order phase transition at ∼4 GPa to suppression of the JT distortion.[9] Later work, however, showed that the phase transition was more likely due to octahedral tilting and that much higher pressures were necessary to compete with the JT distortion.[10] We investigated the behavior of (EDBE)CuCl$_4$ (EDBE = 2,2′-(ethylenedioxy)bis(ethylammonium); Figure 4A) under pressures up to 60 GPa.[11] In addition to the first-order α-to-β phase transition at ∼4 GPa, we observed a previously unreported second-order β-to-γ phase transition at ∼8 GPa. The material's black color and high conductivity in this phase (see the Electronic Effects of Compression discussion) led us to propose that octahedral tilting and bond compression (i.e., at least partial suppression of the JT distortion) resulted in a half-filled d-orbital-based band.

Interlayer Spacing. By tuning the distance between inorganic sheets in 2D perovskites, we could enhance interlayer electronic communication or change the dielectric constant of the organic layers, which strongly influences the photophysical properties of the inorganic layers.[8] The 2D (MA)$_2$PbI$_2$(SCN)$_2$ contains the shortest interlayer spacing for (001) Pb−I perovskites at 9.2901(9) Å (Figure 5A).[22] This distance can be further
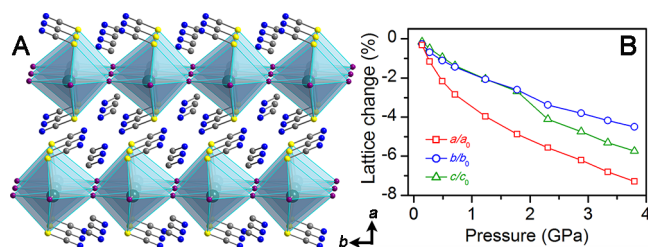

Figure 5. (A) Single-crystal X-ray structure of (MA)$_2$PbI$_2$(SCN)$_2$. Turquoise, purple, yellow, gray, and blue spheres represent Pb, I, S, C, and N, respectively. H atoms were omitted for clarity. (B) Pressure-induced lattice parameter contraction. Adapted from ref 22.

decreased with pressure. At just 2.6 GPa, the interlayer spacing decreases by 6% (Figure 5B), resulting in dramatic optical and electronic changes (see the Color and Optical Absorption and PL discussions).[22]

Amorphization. Another important feature in the high-pressure regime for many halide perovskites is partial amorphization.[13,19,21,24] This results in the disappearance of

most—but not all—crystalline reflections and the appearance of broad baseline signals in diffraction patterns. The photoluminescence of emissive halide perovskites is often quenched in these phases. The nature of the amorphous phases is not fully understood. However, they likely contain aperiodic local lattice distortions in the inorganic sublattice, which results in diffraction peak broadening. This explains the reversibility of the amorphization, wherein the crystalline phases are recovered upon decompression, albeit with slight loss in diffraction intensity.

Electronic Effects of Compression. The optoelectronic properties of halide perovskites strongly depend on the inorganic lattice's pressure response. Bond contraction increases metal halide orbital overlap, thereby increasing electronic band dispersion. Depending on the orientation and symmetry of orbitals within the metal halide octahedra, octahedral tilting may increase or decrease orbital overlap and band dispersion. Partial amorphization, which affects long-range order, also results in prominent electronic effects.

Color. Dramatic color changes are indicators of shifts in electronic properties. Figure 6 shows beautiful examples of
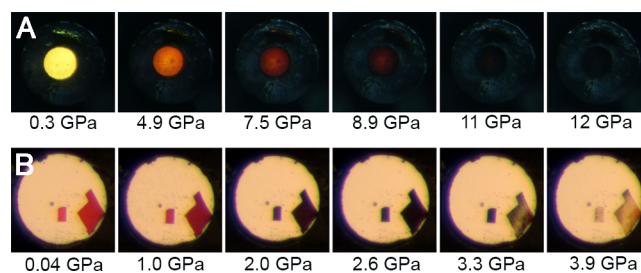

Figure 6. Optical micrographs showing piezochromism in (A) (EDBE)CuCl$_4$ powder and (B) (MA)$_2$PbI$_2$(SCN)$_2$ crystals. Adapted from refs 11 and 22.

piezochromism in halide perovskites.[11,22] Solid (EDBE)CuCl$_4$ transforms from translucent yellow to translucent red-orange during the α-to-β phase transition at ∼4 GPa. Its subsequent second-order β-to-γ phase transition at ∼8 GPa occurs with significant darkening, and at pressures above ∼12 GPa, the perovskite becomes opaque black.[11] A similar change from translucent red to opaque black occurs at a much lower pressure of ∼2.6 GPa in (MA)$_2$PbI$_2$(SCN)$_2$. At pressures above 3.9 GPa, this perovskite becomes translucent yellow, suggesting a widening bandgap.[22] The 3D lead halide perovskites often lighten in color with compression up to ∼4 GPa (as the bandgap increases), commonly followed by darkening above ∼10 GPa (as the bandgap decreases).[13,16,21]

Optical Absorption and Photoluminescence (PL). Pressure-induced structural changes in halide perovskites correlate well with changes in their optical absorption and PL. The high-pressure PL energy allows us to deduce the bandgap of direct-bandgap materials, where the PL results from a radiative band-edge transition. Here we assume no change in Stokes shift with compression. In 2D perovskites, we must assume that both the Stokes shift and exciton binding energy (E_b) do not significantly change with material compression. This is supported by early work on 2D Pb−I perovskites, which showed similar E_b values at both ambient and elevated pressure.[27] Pressure-dependent optical absorption spectra provide a more direct gauge of how the bandgaps of these materials evolve with compression. Importantly, absorption

experiments allow us to track bandgap evolution even at pressures where the PL is quenched or in materials that do not exhibit radiative band-edge transitions.

In $(MA)PbX_3$ (X = Br^- or I^-), increased octahedral tilting likely decreases orbital overlap, thus decreasing band dispersion and increasing the bandgap. Lead halide bond contraction induces the opposite effect by increasing orbital overlap and band dispersion, thereby decreasing the bandgap. This simple explanation is corroborated by PL and absorption spectroscopy[13−17,21,28] and electronic structure calculations.[13,14,17] The PL energy from a $(MA)PbI_3$ single crystal (Figure 7A) shows the
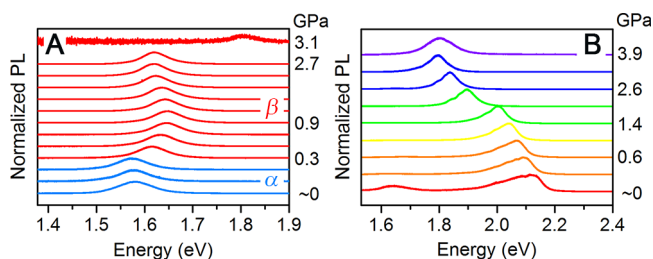

Figure 7. PL from (A) $(MA)PbI_3$ and (B) $(MA)_2PbI_2(SCN)_2$ single crystals upon compression. Adapted from refs 13 and 22.

expected trends based on pressure-induced structural changes. Namely, the PL red shifts correlate with increased metal halide bond compression within the α and β phases, while the pronounced octahedral tilting evident at the onset of the α-to-β phase transition is captured in the abrupt blue shift in PL energy. Though bond contraction likely contributes to the PL red shift with pressure in 2D $(MA)_2PbI_2(SCN)_2$ (Figure 7B), its strong pressure response may also result from decreases in interlayer spacing (see the Interlayer Spacing discussion). This perovskite has an unusually low bandgap for an $n = 1$ Pb−I perovskite of 2.33 eV, which reaches ∼2 eV at a relatively low pressure of 2.6 GPa.[22] In contrast, compression above 24 GPa was required to reach a similar bandgap in $(C_8H_{17}NH_3)_2PbI_4$.[27] This study suggests that compositional tuning can affect large changes in the perovskites' pressure response.

Optical absorption measurements of $(MA)PbI_3$ (Figure 8A) confirm the conclusions from PL experiments. Above 6.0 GPa,
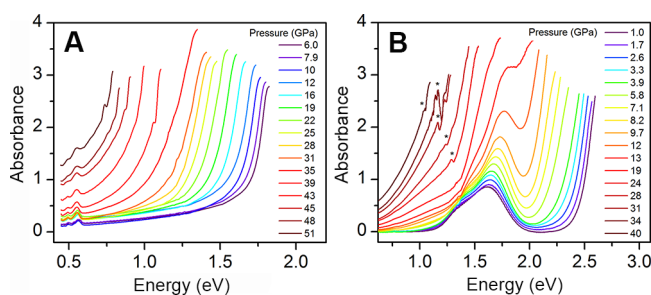

Figure 8. Variable-pressure absorption spectra for (A) $(MA)PbI_3$ and (B) $(EDBE)CuCl_4$. Asterisks denote a detector change. Adapted from refs 36 and 11.

when the PL is quenched,[13] the bandgap continually red shifts with compression. The charge-transfer transition in $(EDBE)CuCl_4$ also red shifts with increasing pressure (Figure 8B), explaining the continuous darkening of this material (Figure 6A). Therefore, lattice compression substantially modulates the bandgap of these insulators and semiconductors.

Lattice compression is also reported to affect the excited-state photophysics of $(MA)PbI_3$. Enhanced carrier lifetime with mild pressure up to 0.3 GPa, along with a sharpening of the absorption onset and bandgap narrowing, has been documented.[17] The increased carrier lifetime (by ca. 70%) was attributed to the removal of mid-bandgap trap states or the formation of shallower traps due to the reduced bandgap. A separate report, however, asserts the opposite effect. Here, carrier lifetimes were reported to decrease with compression up to and past 0.3 GPa.[29] These authors suggest that $(MA)PbI_3$ actually has an indirect bandgap at ambient pressure (resulting from splitting of the conduction band due to spin−orbit coupling or Rashba splitting). They posit that the indirect gap at ambient pressure (ca. 60 meV lower in energy than the direct gap) protects carriers from the fast, direct recombination pathway. Upon moderate compression, they suggest that the bandgap becomes more direct from pressure-induced changes in the local electric field, which reduces the Rashba splitting.[29]

Pressure Effects on Trap States. The mixed halide perovskites $(MA)Pb(Br_xI_{1−x})_3$ ($0.2 < x < 1$) have been considered as absorbers with tunable bandgaps, which could deliver the high voltages required for tandem solar cells.[30] However, high steady-state voltages have been difficult to achieve from devices using these absorbers. We found that these mixed halide perovskites exhibit an instability toward light, manifest in the discrete red shifting of their PL with illumination.[31] We proposed that the material segregates to iodide-rich and bromide-rich domains under extended illumination (Figure 9A), where the iodide-rich domains pin the PL to low energies.[30,31] Halide segregation requires halide mobility. Indeed, related metal halides,[32] and more recently $(MA)PbI_3$,[33] have been shown to be mixed electronic−ionic conductors. We therefore postulated that halide migration could be kinetically suppressed in a stiffer lattice. Alternatively, because halide migration is thought to occur through halide vacancies,[32,33] pressure could change the thermodynamic distribution of lattice defects. Tracking the high-pressure PL of $(MA)Pb(Br_xI_{1−x})_3$ ($0.2 < x < 1$) as a function of irradiation time, we observed that compression below 1 GPa could mitigate the PL red shift (Figure 9C).[13] Therefore, even relatively low pressures may increase the accessible voltages from mixed halide perovskite devices. Interestingly, a new PL band (peak 2 in Figure 9B), whose energy is invariant with light-soaking, appears above the $\alpha−\beta$ phase transition. This peak's energy and its pressure response suggest that it originates from the β phase where halide segregation is suppressed. Recently, higher voltages have been realized in mixed halide, mixed A-site perovskite devices (e.g., $[HC(NH_2)_2]_{0.83}Cs_{0.17}Pb(Br_{0.6}I_{0.4})_3$).[34] Their greater light stability may result from chemical pressure (see the Future Challenges discussion) mimicking the effects of mechanical compression.

Transport Properties. The electronic conductivity of halide perovskites can be substantially tuned with compression. For example, the conductivity of 2D $(EDBE)CuCl_4$ increases by 5 orders of magnitude between 7 and 50 GPa.[11] The conductivities of 3D $(MA)PbBr_3$[35] (up to 25 GPa) and $(MA)SnI_3$[20] (up to 10−20 GPa) have been reported to decrease with compression. Pressure can also greatly increase the conductivity of 3D perovskites. In $(MA)PbI_3$, conductivity increases with compression up to ∼5 GPa, followed by a plateau. Subsequently, we observed a large increase in conductivity (Figure 10A) and decrease in activation energy of conduction (E_a) above ∼30 GPa, culminating in a
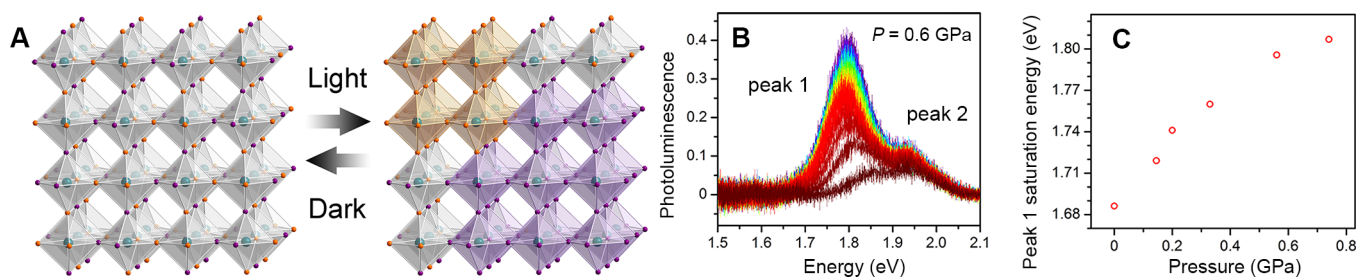
Figure 9. (A) Schematic of halide segregation in mixed halide perovskites. Turquoise, purple, and orange spheres represent Pb, I, and Br atoms, respectively. A-site cations are not shown. (B) PL spectra for $(MA)Pb(Br_{0.6}I_{0.4})_3$ at 0.6 GPa with light soaking, ranging from 0 (dark red) to 150 s (purple). (C) Pressure dependence of the energy to which peak 1 asymptotes with light exposure. (B) and (C) are adapted from ref 13.
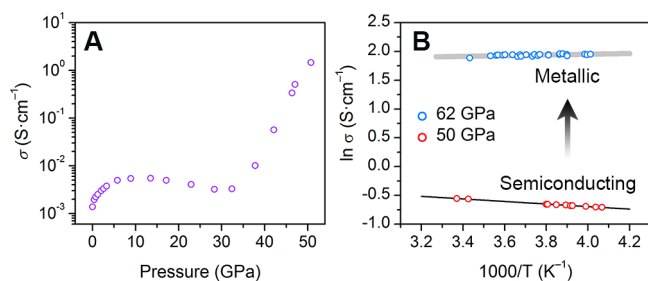

Figure 10. (A) Variable-pressure conductivity (σ) of $(MA)PbI_3$. (B) Temperature dependence of the conductivity in $(MA)PbI_3$. The black line is a fit to the Arrhenius equation, and the gray bar is a guide for the eye. Adapted from refs 13 and 36.

conductivity of 1.5 S·cm^{-1} at 51 GPa with a low E_a of 13.2(3) meV.[13] Decreasing E_a and increasing conductivity suggested the approach of a metallic transition.

Metallization. We recently found that $(MA)PbI_3$ becomes a metal at pressures above 60 GPa through apparent bandgap closure.[36] Metallic behavior was confirmed using reflectivity measurements, which exhibited increasing reflectivity at low frequency, characteristic of free carriers. Furthermore, at 50 GPa, the conductivity increases with increasing temperature, following the Arrhenius behavior exhibited by semiconductors (Figure 10B). However, at 62 GPa, above the metallic transition, the conductivity mildly decreases with increasing temperature, consistent with metallic character. This semiconductor-to-metal transition affords a wholly new electronic platform for this versatile solid.

Metallic oxide perovskites are common, yet all known 2D and 3D halide perovskites have bandgaps of 1−3 eV. Although 3D Sn−I perovskites show metallic behavior,[18,37,38] they have bandgaps of ∼1.3 eV. Here, metallic character arises from facile hole doping at the maximum of the disperse Sn-based valence band.[18,38] To our knowledge, the only other halide perovskites to show metallic behavior at high pressure are the double perovskites $Cs_2Au^IAu^{III}X_6$ (X = Cl$^-$, Br$^-$, or I$^-$).[39] Here, electronic delocalization between the mixed-valence gold centers is thought to contribute to the transport properties.

Outlook. We envision that the study of halide perovskites under pressure will reveal desirable new properties. Synthetic and postsynthetic methods may then be developed to more easily access these effects in technology. As the paradigm of halide−perovskite research shifts from exploration to design, high-pressure studies can direct future synthetic efforts.

Limitations and Opportunities. (i) Limitations: Many pressure-induced changes in halide perovskites (e.g., enhanced conductivity or modified bandgap) are fully reversible upon

decompression, although a recent report showed slight retention of the compression-induced bandgap decrease (of ca. 40 meV) in $[HC(NH_2)_2]PbI_3$.[40] While this reversibility is impressive, it impedes the isolation of materials with favorable high-pressure properties. Even if the high-pressure phases could be kinetically trapped, producing these materials in sufficient scale is still challenging because of the small sample size accommodated in DACs. However, some halide perovskites exhibit significant response even at relatively low pressures, for which larger-scale compression methods are more feasible. *(ii) Opportunities:* The reversibility of pressure-induced effects can

> The reversibility of pressure-induced effects can be an advantage for applications requiring transient changes in electronic properties.

be an advantage for applications requiring transient changes in electronic properties. For example, pressure-induced conductivity in perovskite films could be used to write electronic circuits simply through high-pressure contact, while the circuitry could be erased when the contact is removed. Large changes in conductivity or long-range electronic or magnetic order induced by compression could be employed for rewritable memory storage technologies. Pressure-induced changes in color and electronic conductivity can also be used to register impact and sense stress on perovskite films, serving as early indicators that the underlying substrate has been compromised.

Future Challenges. (i) Using chemical pressure: Understanding the structural basis for pressure-induced changes will aid in the systematic implementation of chemical pressure to permanently realize the effects of mechanical compression. Here, atoms/molecules slightly mismatched in size with the rest of the lattice induce strain. The effects of chemical pressure have been shown to mimic those of mechanical pressure,[41] and theoretical studies have helped relate these two effects.[42] By exploring substitution chemistry, intermolecular interactions, and postsynthetic reactions,[3] we could learn to manipulate chemical pressure to affect desired properties. *(ii) Improving pressure response:* Designing perovskites that respond to technologically accessible pressures is another important goal. Examples include designing 2D perovskites with reduced interlayer spacing, employing more compressible organic cations, and isolating new perovskites that lie close to boundaries in pressure−temperature phase space. *(iii) Characterizing the high-pressure phases:* The high-pressure, partially amorphous phases of halide

perovskites host rich electronic phenomena such as metallic transport properties. The structural changes that occur in these phases should be tracked using alternative methods to standard diffraction experiments, such as X-ray absorption and pair distribution function measurements, which probe more local structural trends, supplemented by theoretical input. *(iv) Accessing metallic transitions:* Pressure-induced metallization of

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halide perovskites is an exciting development that may herald new electronic phenomena such as superconductivity that have so far been restricted to their oxide analogues. Indeed, the electron−phonon coupling exhibited in halide perovskites, coupled to the polarizability of the A-site cations and electronic itinerancy seen in metals, may lead to exotic transport properties. Notably, the softer lattices and templating effects of diverse organic molecules that can structurally fine-tune the inorganic lattice make halide perovskites a veritable playground for manipulating electrons through lattice compression.

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The authors declare no competing financial interest.

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Adam Jaffe studied catalysts for ethanol electrooxidation in fuel cells as an undergraduate with Prof. Andrew Bocarsly at Princeton University. As a Ph.D. candidate with Prof. Karunadasa at Stanford University, his research has encompassed high-pressure, optoelectronic, and energy storage properties of hybrid materials.

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Hemamala Karunadasa did undergraduate research in solid-state chemistry at Princeton University and studied molecular catalysis as a graduate student at the University of California at Berkeley and as a postdoctoral researcher at the California Institute of Technology. Her group at Stanford University synthesizes and studies new hybrid materials that combine the properties of organic small molecules and extended inorganic solids.

REFERENCES

(1) Saparov, B.; Mitzi, D. B. Organic−inorganic perovskites: Structural versatility for functional materials design. *Chem. Rev.* **2016**, *116*, 4558−4596.

(2) Green, M. A.; Ho-Baillie, A.; Snaith, H. J. The emergence of perovskite solar cells. *Nat. Photonics* **2014**, *8*, 506−514.

(3) Smith, I. C.; Smith, M. D.; Jaffe, A.; Lin, Y.; Karunadasa, H. I. Between the sheets: Postsynthetic transformations in hybrid perovskites. *Chem. Mater.* **2017**, *29*, 1868−1884.

(4) Goñi, A. R.; Syassen, K. In *Semiconductors and Semimetals*; Tadeusz, S., William, P., Eds.; Elsevier: Amsterdam, The Netherlands, 1998; Vol. *54*, pp 247−425.

(5) Mao, H. K.; Mao, W. L. *Treatise on Geophysics*; Elsevier: Amsterdam, The Netherlands, 2007; pp 231−267.

(6) Umebayashi, T.; Asai, K.; Kondo, T.; Nakao, A. Electronic structures of lead iodide based low-dimensional crystals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *67*, 155405.

(7) Desjardins, S. R.; Penfield, K. W.; Cohen, S. L.; Musselman, R. L.; Solomon, E. I. Detailed absorption, reflectance, and UV photoelectron spectroscopic and theoretical studies of the charge-transfer transitions of $CuCl_4^{2-}$: Correlation of the square-planar and the tetrahedral limits. *J. Am. Chem. Soc.* **1983**, *105*, 4590−4603.

(8) Smith, M. D.; Pedesseau, L.; Kepenekian, M.; Smith, I. C.; Katan, C.; Even, J.; Karunadasa, H. I. Decreasing the electronic confinement in layered perovskites through intercalation. *Chem. Sci.* **2017**, *8*, 1960−1968.

(9) Moritomo, Y.; Tokura, Y. Pressure-induced disappearance of the in-plane lattice distortion in layered cupric chloride: $(C_2H_5NH_3)_2CuCl_4$. *J. Chem. Phys.* **1994**, *101*, 1763−1766.

(10) Aguado, F.; Rodríguez, F.; Valiente, R.; Itiè, J.-P.; Hanfland, M. Pressure effects on Jahn-Teller distortion in perovskites: The roles of local and bulk compressibilities. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *85*, 100101.

(11) Jaffe, A.; Lin, Y.; Mao, W. L.; Karunadasa, H. I. Pressure-induced conductivity and yellow-to-black piezochromism in a layered Cu−Cl hybrid perovskite. *J. Am. Chem. Soc.* **2015**, *137*, 1673−1678.

(12) Onoda-Yamamuro, N.; Yamamuro, O.; Matsuo, T.; Suga, H. *P-T* phase relations of $CH_3NH_3PbX_3$ (X = Cl, Br, I) crystals. *J. Phys. Chem. Solids* **1992**, *53*, 277−281.

(13) Jaffe, A.; Lin, Y.; Beavers, C. M.; Voss, J.; Mao, W. L.; Karunadasa, H. I. High-pressure single-crystal structures of 3D lead-halide hybrid perovskites and pressure effects on their electronic and optical properties. *ACS Cent. Sci.* **2016**, *2*, 201−209.

(14) Jiang, S.; Fang, Y.; Li, R.; Xiao, H.; Crowley, J.; Wang, C.; White, T. J.; Goddard, W. A.; Wang, Z.; Baikie, T.; et al. Pressure-dependent polymorphism and band-gap tuning of methylammonium lead iodide perovskite. *Angew. Chem., Int. Ed.* **2016**, *55*, 6540−6544.

(15) Capitani, F.; Marini, C.; Caramazza, S.; Postorino, P.; Garbarino, G.; Hanfland, M.; Pisanu, A.; Quadrelli, P.; Malavasi, L. High-pressure behavior of methylammonium lead iodide (MAPbI$_3$) hybrid perovskite. *J. Appl. Phys.* **2016**, *119*, 185901.

(16) Szafrański, M.; Katrusiak, A. Mechanism of pressure-induced phase transitions, amorphization, and absorption-edge shift in photovoltaic methylammonium lead iodide. *J. Phys. Chem. Lett.* **2016**, *7*, 3458−3466.

(17) Kong, L.; Liu, G.; Gong, J.; Hu, Q.; Schaller, R. D.; Dera, P.; Zhang, D.; Liu, Z.; Yang, W.; Zhu, K.; et al. Simultaneous band-gap narrowing and carrier-lifetime prolongation of organic−inorganic trihalide perovskites. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 8910−8915.

(18) Takahashi, Y.; Hasegawa, H.; Takahashi, Y.; Inabe, T. Hall mobility in tin iodide perovskite $CH_3NH_3SnI_3$: Evidence for a doped semiconductor. *J. Solid State Chem.* **2013**, *205*, 39−43.

(19) Lee, Y.; Mitzi, D. B.; Barnes, P. W.; Vogt, T. Pressure-induced phase transitions and templating effect in three-dimensional organic-inorganic hybrid perovskites. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *68*, 020103.

(20) Lü, X.; Wang, Y.; Stoumpos, C. C.; Hu, Q.; Guo, X.; Chen, H.; Yang, L.; Smith, J. S.; Yang, W.; Zhao, Y.; et al. Enhanced structural stability and photo responsiveness of $CH_3NH_3SnI_3$ perovskite via pressure-induced amorphization and recrystallization. *Adv. Mater.* **2016**, *28*, 8663−8668.

(21) Wang, L.; Wang, K.; Zou, B. Pressure-induced structural and optical properties of organometal halide perovskite-based formamidinium lead bromide. *J. Phys. Chem. Lett.* **2016**, *7*, 2556−2562.

(22) Umeyama, D.; Lin, Y.; Karunadasa, H. I. Red-to-black piezochromism in a compressible Pb−I−SCN layered perovskite. *Chem. Mater.* **2016**, *28*, 3241−3244.

(23) Mattern, E.; Matas, J.; Ricard, Y.; Bass, J. Lower mantle composition and temperature from mineral physics and thermodynamic modelling. *Geophys. J. Int.* **2005**, *160*, 973−990.

(24) Swainson, I. P.; Tucker, M. G.; Wilson, D. J.; Winkler, B.; Milman, V. Pressure response of an organic−inorganic perovskite: Methylammonium lead bromide. *Chem. Mater.* **2007**, *19*, 2401−2405.

(25) Glazer, A. The classification of tilted octahedra in perovskites. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *28*, 3384−3392.

(26) Murayama, C.; Iye, Y.; Enomoto, T.; Môri, N.; Yamada, Y.; Matsumoto, T.; Kubo, Y.; Shimakawa, Y.; Manako, T. Correlation between the pressure-induced changes in the Hall coefficient and T_c in superconducting cuprates. *Phys. C* **1991**, *183*, 277−285.

(27) Matsuishi, K.; Suzuki, T.; Onari, S.; Gregoryanz, E.; Hemley, R. J.; Mao, H. K. Excitonic states of alkylammonium lead-iodide layered perovskite semiconductors under hydrostatic pressure to 25 GPa. *Phys. Status Solidi B* **2001**, *223*, 177−182.

(28) Matsuishi, K.; Ishihara, T.; Onari, S.; Chang, Y. H.; Park, C. H. Optical properties and structural phase transitions of lead-halide based inorganic−organic 3D and 2D perovskite semiconductors under high pressure. *Phys. Status Solidi B* **2004**, *241*, 3328−3333.

(29) Wang, T.; Daiber, B.; Frost, J. M.; Mann, S. A.; Garnett, E. C.; Walsh, A.; Ehrler, B. Indirect to direct bandgap transition in methylammonium lead halide perovskite. *Energy Environ. Sci.* **2017**, *10*, 509−515.

(30) Slotcavage, D. J.; Karunadasa, H. I.; McGehee, M. D. Light-induced phase segregation in halide-perovskite absorbers. *ACS Energy Lett.* **2016**, *1*, 1199−1205.

(31) Hoke, E. T.; Slotcavage, D. J.; Dohner, E. R.; Bowring, A. R.; Karunadasa, H. I.; McGehee, M. D. Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics. *Chem. Sci.* **2015**, *6*, 613−617.

(32) Kuku, T. A.; Salau, A. M. Electrical conductivity of $CuSnI_3$, $CuPbI_3$ and $KPbI_3$. *Solid State Ionics* **1987**, *25*, 1−7.

(33) Yang, T.-Y.; Gregori, G.; Pellet, N.; Grätzel, M.; Maier, J. The significance of ion conduction in a hybrid organic−inorganic lead-iodide-based perovskite photosensitizer. *Angew. Chem., Int. Ed.* **2015**, *54*, 7905−7910.

(34) McMeekin, D. P.; Sadoughi, G.; Rehman, W.; Eperon, G. E.; Saliba, M.; Hörantner, M. T.; Haghighirad, A.; Sakai, N.; Korte, L.; Rech, B.; et al. A mixed-cation lead mixed-halide perovskite absorber for tandem solar cells. *Science* **2016**, *351*, 151−155.

(35) Wang, Y.; Lü, X.; Yang, W.; Wen, T.; Yang, L.; Ren, X.; Wang, L.; Lin, Z.; Zhao, Y. Pressure-induced phase transformation, reversible amorphization, and anomalous visible light response in organolead bromide perovskite. *J. Am. Chem. Soc.* **2015**, *137*, 11144−11149.

(36) Jaffe, A.; Lin, Y.; Mao, W. L.; Karunadasa, H. I. Pressure-induced metallization of the halide perovskite $(CH_3NH_3)PbI_3$. *J. Am. Chem. Soc.* **2017**, *139*, 4330−4333.

(37) Mitzi, D. B.; Feild, C. A.; Harrison, W. T. A.; Guloy, A. M. Conducting tin halides with a layered organic-based perovskite structure. *Nature* **1994**, *369*, 467−469.

(38) Chung, I.; Song, J.-H.; Im, J.; Androulakis, J.; Malliakas, C. D.; Li, H.; Freeman, A. J.; Kenney, J. T.; Kanatzidis, M. G. $CsSnI_3$:

Semiconductor or metal? High electrical conductivity and strong near-Infrared photoluminescence from a single material. High hole mobility and phase-transitions. *J. Am. Chem. Soc.* **2012**, *134*, 8579−8587.

(39) Kojima, N. Gold valence transition and phase diagram in the mixed-valence complexes, $M_2[Au^IX_2][Au^{III}X_4]$ (M = Rb, Cs; X = Cl, Br, and I). *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1445−1460.

(40) Liu, G.; Kong, L.; Gong, J.; Yang, W.; Mao, H.-k.; Hu, Q.; Liu, Z.; Schaller, R. D.; Zhang, D.; Xu, T. Pressure-induced bandgap optimization in lead-based perovskites with prolonged carrier lifetime and ambient retainability. *Adv. Funct. Mater.* **2017**, *27*, 1604208.

(41) Morón, M. C.; Palacio, F.; Clark, S. M. Pressure-induced structural phase transitions in the $AMnF_4$ series (A = Cs, Rb, K) studied by synchrotron X-ray powder diffraction: Correlation between hydrostatic and chemical pressure. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 7052−7061.

(42) Luty, T.; Eckhardt, C. J. General theoretical concepts for solid state reactions: Quantitative formulation of the reaction cavity, steric compression, and reaction-induced stress using an elastic multipole representation of chemical pressure. *J. Am. Chem. Soc.* **1995**, *117*, 2441−2452.