

# Pressure-induced emission from low-dimensional perovskites

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White light emitting diodes from a single emitter is of significance in application of illumination and image display because of avoiding the color instability in devices with multiple emitters<sup>[1, 2]</sup>. Recently, as a single emitter, low-dimensional halide perovskites have drawn great attention for their broadband solid-state lighting based on the radiative recombination of self-trapped excitons (STEs) and excellent device stability<sup>[3–8]</sup>. The dimensionality reduction could effectively enhance the deformability of octahedral framework and thus electron–phonon coupling strength, facilitating exciton self-trapping. However, low-dimensional perovskites cannot satisfy the requirement of device commercialization due to the rare achievement of high photoluminescence quantum yield<sup>[9]</sup>. Developing an effective strategy to improve the emission and elucidating the underlying mechanism have become an urgent need.

Pressure, produced by diamond anvil cell (DAC, Fig. 1(a)), could effectively shorten interatomic distances and profoundly modify electronic orbitals and bonding patterns, generating new structures with novel properties<sup>[10]</sup>. Recently, high pressure has been regarded as the one of the “Top-Ten Emerging Technologies in Chemistry”, and no longer a small field, which accelerates the development of science and technology and enhances luminescence and superconductivity<sup>[11]</sup>. Therefore, pressure is expected to greatly improve the luminescent performance without altering the component of the material. In 1992, Drickamer *et al.* observed pressure-induced emission enhancement (PIEE), i.e., a solid-state luminogen gave enhanced emission upon compression<sup>[12]</sup>. Zou *et al.* first reported pressure-induced emission (PIE) from zero-dimensional all-inorganic halide perovskite, Cs<sub>4</sub>PbBr<sub>6</sub> nanocrystals (NCs), i.e., an unexpected broad emission was generated by pressing an non-emissive sample (Figs. 1(b) and 1(c))<sup>[13]</sup>. The exotic PIE occurred at 3.01 GPa, and Cs<sub>4</sub>PbBr<sub>6</sub> NCs experienced a reversible phase transition from a rhombohedral phase to a monoclinic phase, accompanied by a significant distortion of [PbBr<sub>6</sub>]<sup>4-</sup> octahedra. This change enhances the wavefunction overlap between the excited state and the ground state, promoting the dipole moment compared to the ambient-pressure state (Fig. 1(d)). Meanwhile, the electron–phonon coupling strength associated with the Huang–Rhys factor is enhanced under high pressure, which effectively strengthens the binding energy of STEs and inhibits

the transformation from STEs to bound excitons. Finally, under stimulus of external pressure, the radiative recombination of STEs generates the exotic broad emission. Here, the concept of PIE refers to a novel phenomenon, i.e., a non-luminescent material gives emission upon compression. In fact, PIE could completely cover the description of PIEE. Such PIE phenomenon was also observed in one-dimensional Sn-based perovskites (Figs. 1(e) and 1(f)), reported by Shi *et al.*<sup>[14]</sup>. Ma *et al.* proved that the distortion determined PIE, and the greater the zigzag distortion, the more remarkable the PIE (Fig. 1(g))<sup>[15]</sup>.

The quenched PIE perovskites generally recover to the initial non-emissive state, which significantly inhibits their practical applications. In this regard, Fu *et al.* recently proposed a new strategy to keep inorganic octahedral distortion through the introduction of steric hindrance of appropriate organic cations. The high-efficiency emission of quenched two-dimensional perovskite, (PEA)<sub>2</sub>PbCl<sub>4</sub> NCs (PEA<sup>+</sup> = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>), was achieved as anticipated (Figs. 2(a)–2(c)). This work not merely provided a pathway to yield stable perovskite with high emission *via* a “clean” pressure treatment, but also enabled an obvious color change from “warm” (4403 K) to “cold” white light (14 295 K) (Fig. 2(d))<sup>[16]</sup>. Furthermore, retention of PIE was also realized in microtubules (MTs) of zero-dimensional hybrid halide (4-AMP)<sub>2</sub>ZnBr<sub>4</sub> (4-AMP<sup>+</sup> = C<sub>5</sub>H<sub>7</sub>N<sub>2</sub><sup>+</sup>) (Fig. 2(e)). Joint experimental and theoretical analyses indicate irreversible electronic transition induced by the steric hindrance is responsible for the irreversible optical properties (Figs. 2(f) and 2(g))<sup>[17]</sup>.

In conclusion, the pressure causes distorted octahedra within low-dimensional perovskites to affect STE behavior and generates PIE. The PIE can be modulated by introducing steric hindrance from appropriate organic cations. There is still a large room for adjusting the steric effect *via* tuning the structure and size of organic cations.

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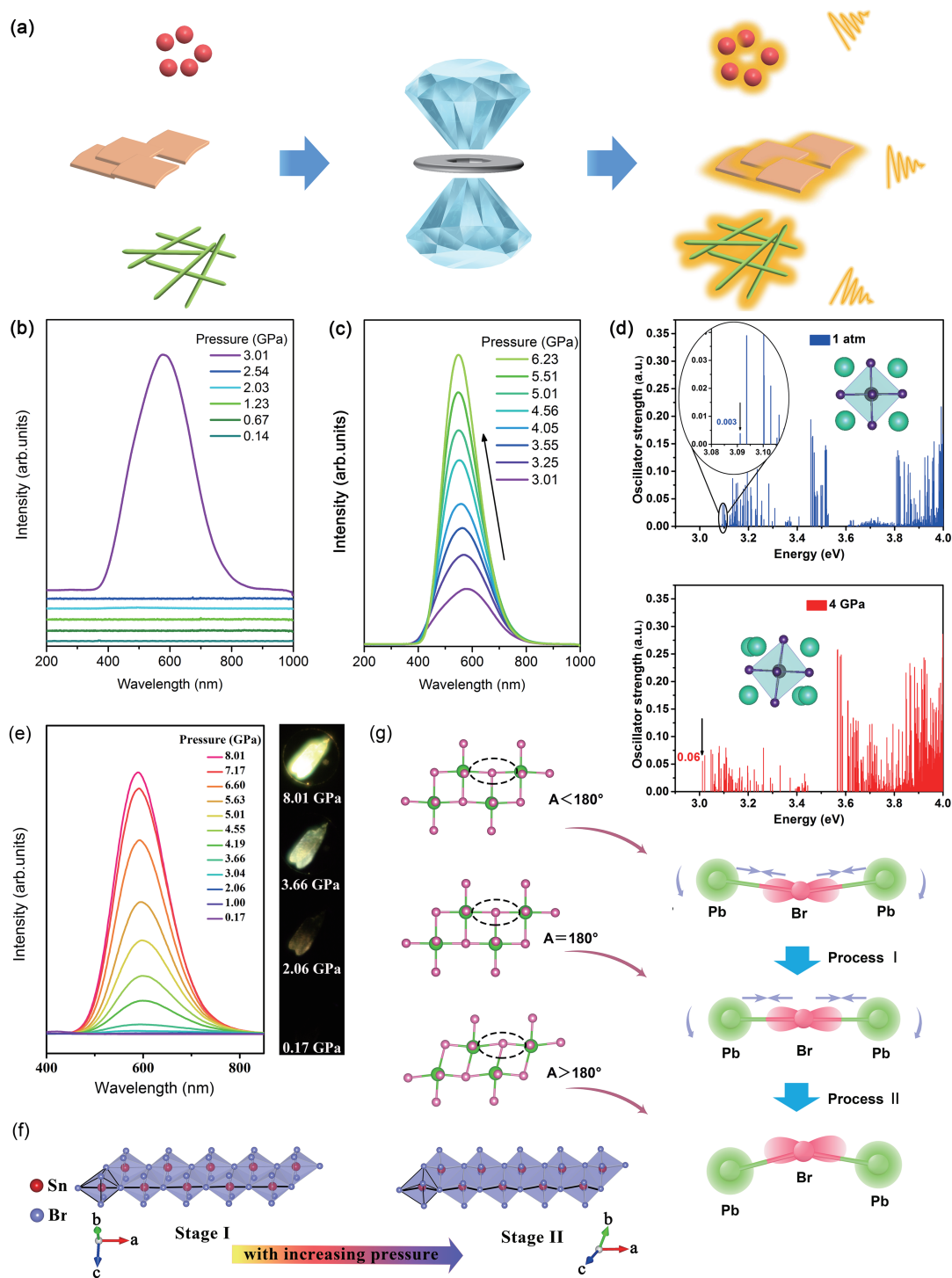


Fig. 1. (Color online) (a) Schematic diagram of a symmetric DAC apparatus used in the high-pressure experiments for 0-, 1- and 2D perovskites. (b) and (c) High-pressure emission from Cs<sub>4</sub>PbBr<sub>6</sub> NCs. (d) Calculated absorption oscillator strength by using excited-state structure associated with STE at 1 atm and 4 GPa, respectively. Reproduced with permission<sup>[13]</sup>, Copyright 2018, Springer Nature. (e) Pressure-dependent PL spectra for 1D perovskite C<sub>4</sub>N<sub>2</sub>H<sub>14</sub>SnBr<sub>4</sub>. (f) Transformation of C<sub>4</sub>N<sub>2</sub>H<sub>14</sub>SnBr<sub>4</sub> under high pressure. Stage I and stage II show octahedral chains before and after the phase transition, respectively. Reproduced with permission<sup>[14]</sup>, Copyright 2019, American Chemical Society. (g) Schematic illustrations of Pb–Br–Pb bond angle and Pb–Br bond length within octahedral framework before and after phase transition. Pb 6s orbital and Br 4p orbital are represented by light green sphere and red spindle, respectively. Reproduced with permission<sup>[15]</sup>, Copyright 2020, Wiley Publishing Group.

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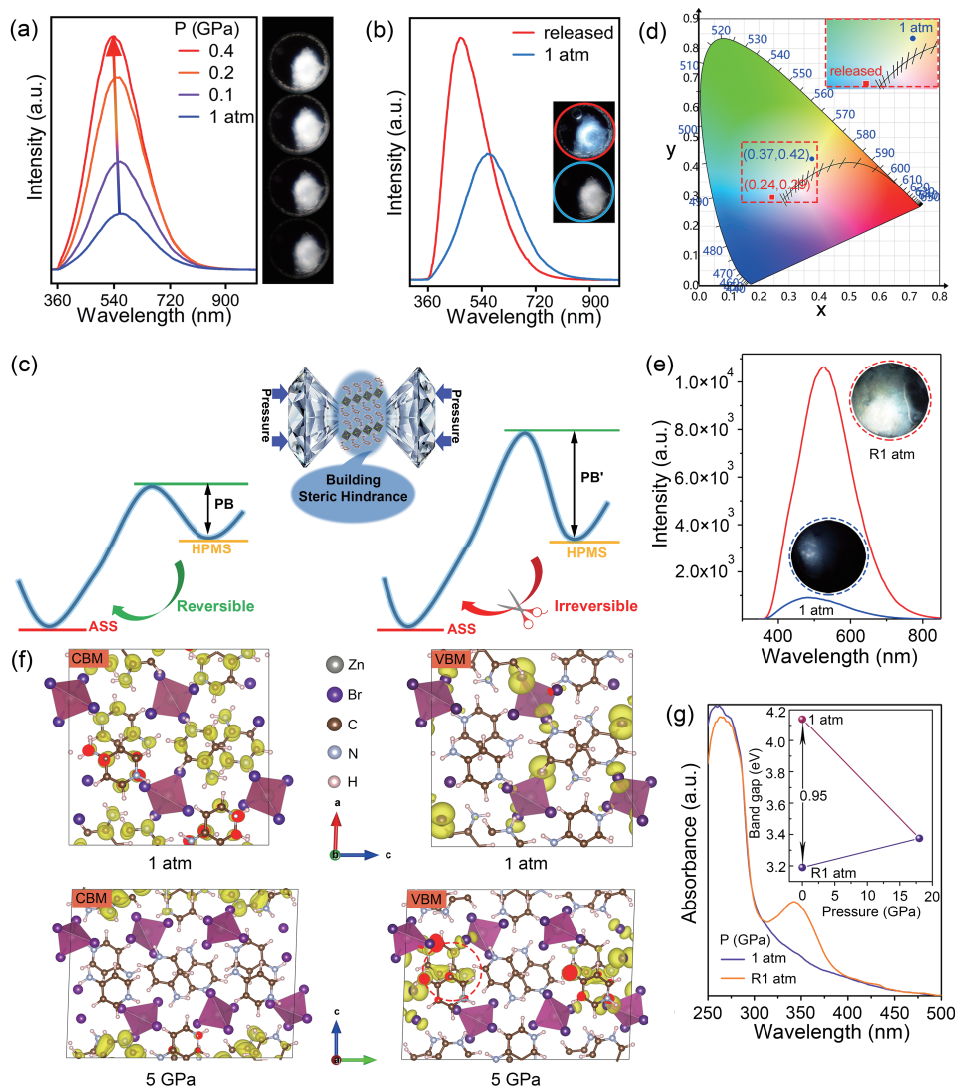


Fig. 2. (Color online) (a) Evolution of PL spectra and microphotographs under pressures from 1 atm to 0.4 GPa. (b) PL spectra for  $(\text{PEA})_2\text{PbCl}_4$  NCs at 1 atm and after pressure release; inset shows the corresponding photographs. (c) Illustrated mechanism of PIE retention affected by steric hindrance of organic cation. ASS: atmospheric stable phase; HPMS: high-pressure metastable state; PB: potential barrier; PB': increased potential barrier. (d) Chromaticity coordinate diagram at 1 atm and after pressure release. Reproduced with permission<sup>[16]</sup>, Copyright 2021, Wiley Publishing Group. (e) PL spectra and photographs for  $(4\text{-AMP})_2\text{ZnBr}_4$  MTs (blue: atmospheric pressure; red: pressure removed). (f) Calculated partial charge density located on CBM and VBM at 1 atm and 5 GPa. (g) UV/Vis absorption spectra at 1 atm and after removal of 18.01 GPa pressure. Reproduced with permission<sup>[17]</sup>, Copyright 2021, Wiley Publishing Group.

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