Manipulating Emission Enhancement and Piezochromism in Two-Dimensional Organic–Inorganic Halide Perovskite [(HO)(CH₂)₂NH₃]₂PbI₄ by High Pressure

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Two-dimensional (2D) organic–inorganic halide perovskites present remarkable stability and diversity and are promising alternatives to their three-dimensional (3D) counterparts. The 2D halide perovskite [(HO)(CH₂)₂NH₃]₂PbI₄ (ETA₂PbI₄) is regarded as a superior moisture-stable “smooth” perovskite because of distinct hydrogen-bond networks that connect adjacent organic–inorganic layers. However, effectively engineering the optical properties of ETA₂PbI₄ for practical applications still represents considerable challenges. Herein, we studied the effect of pressure on the optical characteristics and crystalline structure of ETA₂PbI₄ through a diamond anvil cell. The emission was enhanced four times at 1.5 GPa and was accompanied by a photoluminescence (PL) peak that became more symmetric, which was attributed to pressure-suppression nonradiative recombination and an increase in exciton binding energy. Moreover, the red shift of the PL peak from 542 to 674 nm was continuous at a rate of 14.4 nm/GPa with pressure up to 9.2 GPa. Meanwhile, the optical micrographs showed visualized piezochromism. High-pressure in situ synchrotron X-ray diffraction (XRD), Raman measurements, and first-principles calculations indicated a distortion of the Pb–I–Pb bond angle and the Pb–I bond length leading to this series of transformations. Our findings demonstrate that 2D halide ETA₂PbI₄ is a prospective candidate for pressure sensors.

Keywords: two-dimensional perovskite, emission enhancement, piezochromism, high pressure, band gap red shift
Introduction

The reduced-dimensionality perovskites, especially the two-dimensional (2D) organic-inorganic halide perovskites, have become the “next big thing” in emerging hybrid halide perovskites owing to their excellent tunability and photophysical properties.\(^1\)\(^6\) In strictly 2D organic–inorganic perovskite (A)\(_2\)BX\(_4\), where the large (A)\(^+\) cations divide the infinite inorganic layers, the most common B-site cations are Pb\(^{2+}\), and the X-site cations typically are Cl\(^-\), Br\(^-\), or I\(^-\) anions.\(^7\)\(^8\) In this case, each of the active layers is an infinite 2D sheet of the corner-sharing PbX\(_6\) octahedra.\(^9\) Through their unique crystal structures, quantum confinement leads to strong excitonic effects, therefore, strong photoluminescence (PL) was observed at room temperature.\(^10\) The uniform and stable emission spectra perovskite is the ideal material for making perovskite light-emitting diodes (LEDs).\(^11\) Moreover, 2D perovskites possess significant light absorption in the visible region which makes them a likely light absorber for photovoltaic applications.\(^12\) ETA\(_2\)PbI\(_4\) (ETA = (HO)\((\text{CH}_2)_{2}\text{NH}_3\)\(^+\)) is a unique organic–inorganic hybrid perovskite because it consists of alcohol-based bifunctional ammonium ions.\(^13\) The strong Coulomb interactions within the ETA organic layer are attributed to the extremely smooth crystal surface of ETA\(_2\)PbI\(_4\). Therefore, ETA\(_2\)PbI\(_4\) is considered a “smooth” 2D halide perovskite, which is less sensitive to ambient moisture and exhibits a considerable low dark current.\(^15\) However, it is essential to adjust the band gap in a wide range to realize PL tunability in this 2D hybrid perovskite.

Pressure is a powerful and convenient strategy to alter the crystalline structure and electronic properties of 2D perovskite materials that are sometimes inaccessible by chemical tuning.\(^16\)\(^21\) Depending on the applied pressure, the (BA)\(_2\)(MA)\(_n\)−PbI\(_{3n+1}\) \(_{n+1}\) homologous series shows typical structural transition, which is accompanied by noticeable transformation in the optical properties of these materials.\(^22\)\(^23\) The model (EDBE)CuCl\(_4\) undergoes an α-to-β phase transition, triggering a color change from yellow to orange when pressure increases from 0.3 to 4.9 GPa.\(^24\) These results provided us a basic understanding of the relationship between crystalline structure and optical properties.\(^25\)\(^33\) However, most of these materials are limited by a pressure-induced decrease in PL, which limits their potential applications in optical devices.\(^34\) Despite this, controlling pressure to effectively adjust the band gap and PL increase of ETA\(_2\)PbI\(_4\) remains a particularly promising approach.

In this work, we report the evolution of the optical properties of 2D organic-inorganic halide perovskite ETA\(_2\)PbI\(_4\) upon high-pressure processing. High-pressure PL spectra, optical micrographs, and UV–Vis absorption indicated the distinct piezochromism of the ETA\(_2\)PbI\(_4\) crystal, exhibiting a red shift at approximately 132 nm from the initial 542 to 674 nm at 9.2 GPa. Furthermore, pressure-induced emission was enhanced up to 1.5 GPa resulting from the pressure-suppression non-radiative recombination and the increase in exciton binding energy. The XRD data and Raman spectra of ETA\(_2\)PbI\(_4\) upon compression were obtained to trace the high-pressure changes of the inorganic [PbI\(_6\)]\(^{12+}\) octahedra. The achieved narrow emission with high color purity is favorable for applications of perovskite, which may prove a powerful candidate for pressure sensors at extreme conditions.

Results and Discussion

The pressure-dependent PL spectra were recorded up to 10.3 GPa (Figure 1). Under ambient conditions, ETA\(_2\)PbI\(_4\) shows a sharp and narrow green-free exciton emission centered at 542 nm with full width at half maximum of 24 nm (Supporting Information Figure S1) due to remarkable quantum confinement effects. Meanwhile, the low-energy PL tail of the ETA\(_2\)PbI\(_4\) PL spectrum was ascribed to the radiative recombination of trap states.\(^21\) Intriguingly, ETA\(_2\)PbI\(_4\) PL intensity was enhanced by four times from 1 atm to 1.5 GPa (Figure 1a), which was accompanied by a more symmetrical PL emission peak (Supporting Information Figure S2). Upon further compression, the PL intensity gradually decreased until it completely disappeared at 10.3 GPa (Figure 1a). Upon decompression, the PL spectra returned to its original shape and position, but the PL intensity was slightly weaker than its atmospheric pressure state (Supporting Information Figure S4). The emission spectra showed a wide range of pressure-induced peak change throughout the compression process (Figure 1b).

A series of optical photographs clearly reveal the varying trend of the ETA\(_2\)PbI\(_4\), and the following sequence could be easily visualized by the naked eyes: green → yellow → orange → red (Figure 1b). The PL emission peak of the ETA\(_2\)PbI\(_4\) crystal can be tuned at a rate of 14.4 nm/GPa upon compression (Figure 1c). Furthermore, the chromaticity coordinates of PL upon compression from 1 atm to 9.2 GPa are shown in Figure 1d. The emission at 1 atm belongs to the green component (0.34, 0.64). At 9.2 GPa, the emission moved toward the monochromatic red light (0.70, 0.29). Compression resulted in high color purity and colorful PL modulation, which are favorable conditions for the development of pressure sensors.\(^35\)\(^36\) Consequently, we also used pressure to tune the chromaticity of emission, which facilitates the use of ETA\(_2\)PbI\(_4\) as a pressure sensor with ultrasensitivity to pressure in the low-pressure regime (<8 GPa).

The evolution process of the ETA\(_2\)PbI\(_4\) band gap was obtained by UV–Vis absorption spectroscopy. At ambient conditions, a steep absorption edge was observed at approximately 553 nm and showed remarkable red shifts...
when the pressure reached 8.0 GPa (Figure 2a). The
extraordinary piezochromism transition of ETA2PbI4 is
evident in optical micrographs (Figure 2b). The band gap
of the material was estimated by extrapolating the linear
portion of \((\alpha d\nu)^2\) versus the \(h\nu\) curve, where
\(\alpha\) is the absorption coefficient, \(d\) is the sample thickness, and \(h\nu\)
is the photon energy (Figure 2c). ETA2PbI4 exhibited a
direct gap of 2.24 eV at ambient conditions consistent
with a previous report.13 With increasing pressure, the
band gap of ETA2PbI4 obviously narrowed by 0.39 eV at
8.0 GPa, suggesting that the band gap of the 2D
organic–inorganic halide perovskite is signifi-
cantly mod-
ified by high pressure.

We obtained the in situ high-pressure angle-dispersive
X-ray diffraction (ADXRD) patterns of ETA2PbI4 to
investigate the correlation between the optical prop-
ties and structural variations of ETA2PbI4 (Figure 3a).
Rietveld refinement results of the XRD data at ambient
conditions showed that ETA2PbI4 possessed a mono-
clinic system with the \(P2_1/c\) space group; the lattice
parameters were \(a = 10.22(1) \ \text{Å},\ \beta = 8.04(1) \ \text{Å},\ \text{and}\ c = 8.93(2) \ \text{Å}, \ \beta = 100.27(3)°\) (Supporting Information
Figure S6).13 Figure 3b shows the layered crystalline
structure of ETA2PbI4 along the crystallographic \(b\) axis.
It was formed by alternating sheets of the corner-sharing
PbI6 octahedra and the organic (ETA) cation layers. Two
continuous inorganic octahedral layers move slightly
along the \(a\) axis, and the interlayer I–I bond was very
short approximately along the \(c\) axis. Within the [PbI6]4–
cluster, Pb–I bonds could be divided into two groups: four
investigate the high-pressure behavior of inorganic \( [\text{Pbl}_6]^{3-} \) octahedra, we analyzed ETA\( _2\text{Pbl}_4 \) crystal by Raman spectroscopy, which was consistent with the high-pressure ADXRD result (Supporting Information Figure S8).

We also investigated the evolution of the cell parameters and volume (Supporting Information Figure S9) to further analyze the structural evolution of ETA\( _2\text{Pbl}_4 \). Crystal lattice parameters and volumes of ETA\( _2\text{Pbl}_4 \) were stably and continuously compressed before occurrence of the severely disordered crystallinity. It was found that the deformation \( \Delta a \sim 1.13 \text{ Å} \) was bigger than \( \Delta b \sim 0.75 \text{ Å} \) and \( \Delta c \sim 0.87 \text{ Å} \) under quasi-hydrostatic pressure at 13.0 GPa. Moreover, the deformation percentage along the \( a \) axis (11.1%) was greater than the \( b \) axis (8.3%) and the \( c \) axis (9.7%), with an average 24% decrease. As such, clear anisotropic compression may correspond to the sandwich structure made up of alternately connected organic and inorganic layers. Moreover, the experimental pressure–volume (\( P–V \)) data (Supporting Information Figure S9b) obtained from atmospheric conditions to 13.0 GPa were fitted by utilizing the third-order Birch-Murnaghan equation of state. The fitting bulk modulus \( (K_0) \) of ETA\( _2\text{Pbl}_4 \) was 22.3 GPa, comparable to that of other 2D halide perovskites. The compressibility of ETA\( _2\text{Pbl}_4 \) is obviously smaller than that of its analog 3D perovskites (13.6 GPa of MAPbI\(_3\)). Therefore, 2D perovskite ETA\( _2\text{Pbl}_4 \) is harder and more resistant to pressure than 3D perovskites.

First-principles calculations were performed to investigate the variations of the electronic band structure upon compression, calculated electronic band structure is essential to fully understand the interaction between crystal structure and excitonic bands under high pressure. The results indicate that ETA\( _2\text{Pbl}_4 \) possesses a direct band gap of 1.78 eV at ambient conditions, and the band gap shrinks continuously with increasing pressure up to 8.0 GPa (Figure 4c), which is consistent with the results of our experiments. The valence band maximum (VBM) is mainly comprised of Pb 6s states with contribution of I 5p states. Simultaneously, the conduction band minimum (CBM) is mainly formed by Pb 6p orbitals with contribution of I 5s states (Supporting Information Figure S10). Upon compression, all the Pb–I–Pb angles showed a slight compression (Figure 4a and Supporting Information Table S1) because of the tilting and rotation of \([\text{Pbl}_6]^{3-}\) inorganic octahedra relative to its adjacent octahedra along the \( a \) axis. Meanwhile, the bridging Pb–I bonds and terminal Pb–I\(_2\) bonds were gradually reduced (Figure 4b and Supporting Information Table S2). As such, an increasing electronic band dispersion accompanied rising VBM and falling CBM (Figures 4d and 4e). Therefore, the band gap exhibits a remarkable decrease under 8.0 GPa.

Under lower pressure, the well thickness (\( L \)) showed obvious decrease (Supporting Information Figure S11).
caused by the increase of dielectric confinement due to the negative correlation between L and dielectric confinement. Given that the exciton binding energy is positively correlated with the dielectric confinement, the exciton binding energy increase led to the PL enhancement of ETA$_2$PbI$_4$ under mild pressure. In addition, the more symmetrical PL peak ascribed to pressure-suppressed carrier trapping caused the decrease of the

**Figure 3**  (a) Representative ADXRD of ETA$_2$PbI$_4$ upon compression up to 20.2 GPa. (b) Crystal structure of ETA$_2$PbI$_4$ at ambient conditions, viewed along the b axis. Gray, violet, brown, silver, red, and pink spheres represent Pb, I, C, N, O, and H atoms, respectively. (c) Distorted Pb–I inorganic framework layer at ambient condition, viewed along the a axis. ADXRD, angle-dispersive X-ray diffraction.

**Figure 4**  (a) Schematic illustrations of Pb–I–Pb bond angle within inorganic octahedral framework upon compression. (b) Schematic illustrations of Pb–I bond length within PbI$_6$ octahedral framework upon compression. (c) First-principles calculated band gap for ETA$_2$PbI$_4$ at different pressures. (d and e) Electronic band structure for ETA$_2$PbI$_4$ under ambient conditions and 8.0 GPa, respectively.
nonradiative recombination, which also triggers the enhanced emission.47 As a result, there was a four times PL enhancement of \( \text{ETA}_2\text{PbI}_4 \) observed under 1.5 GPa. Above 1.5 GPa, although \( L \) still decreased, the pressure-induced suppression effect on the PL began to dominate the emission process, which was mainly caused by the structural disorder and which resulted in slow and nonlinear PL weakening.20,48

Conclusion

The pressure-engineered crystalline structure and optical properties of \( \text{ETA}_2\text{PbI}_4 \) were systematically studied with a symmetric diamond anvil cell (DAC) apparatus. The perovskite crystal exhibited distinct enhancement of PL intensity and narrowing of band gap when pressure was applied. High-pressure PL micrographs and UV–Vis absorption micrographs indicated the distinctive piezochromism of \( \text{ETA}_2\text{PbI}_4 \) crystal. Synthetic experiments containing in situ high-pressure ADXRD and Raman measurements indicated that \( \text{ETA}_2\text{PbI}_4 \) crystal experienced remarkable distortion of the \([\text{PbI}_6]^{4-}\) octahedral. Our work provides supplementary information on the intrinsic characteristics of 2D organometal halide perovskites. The pressure-induced distinct PL color change allows the possible use of \( \text{ETA}_2\text{PbI}_4 \) in pressure fiber optic sensors and photovoltaic applications.

Supporting Information

Supporting Information is available.

Conflict of Interest

The authors declare no competing financial interests.

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References


