Synthesis of Two-Dimensional CsPb$_2$X$_5$ (X = Br and I) with a Stable Structure and Tunable Bandgap by CsPbX$_3$ Phase Separation

Mei Li, Shang Peng, Shiyu Fang, Yu Gong, Dongliang Yang, Kejun Bu, Bingyan Liu, Hui Luo, Songhao Guo, Junlong Li, Hao Wang, Yufeng Liu, Sheng Jiang, Chuanlong Lin, * and Xujie Lü *

**ABSTRACT:** Perovskite-related materials with various dimensionalities have attracted sustained attention owing to their extraordinary electronic and optoelectronic properties, but it is still challenging in the synthesis of compounds with desired compositions and structures. Herein, a two-dimensional (2D) CsPb$_2$I$_4$ perovskite has been synthesized by the conversion of CsPbI$_3$ at high-pressure and high-temperature (high P–T) conditions, which is quenchable at ambient conditions. In situ synchrotron X-ray diffraction shows that high-pressure monoclinic CsPbI$_3$ converts into tetragonal CsPbI$_4$, and cubic CsI at 8.7 GPa upon heating from 644 to 666 K. Keeping the tetragonal structure stable, CsPbI$_4$ exhibits tunable optical properties with the bandgap changing from $\sim 2.4$ eV at ambient pressure to $\sim 1.4$ eV at 36.9 GPa. Further experiments demonstrate similar structural evolution in the typical three-dimensional CsPbBr$_3$ perovskite into 2D CsPb$_2$Br$_5$ at high P–T conditions, indicating that the conversion of CsPbX$_3$ (X = Br and I) into CsPb$_2$X$_5$ is ubiquitous.

Halide perovskites, possessing flexible lattices and exceptional optoelectronic properties, have achieved remarkable performance in the applications of solar cells, photodetectors, and light-emitting diodes (LEDs) but still suffer from problems, like the instability of ionic lattices. Two-dimensional (2D) inorganic CsPb$_2$X$_5$ as a derivative of CsPbX$_3$ perovskite, has attracted increasing attention owing to its unique optical properties and quantum confinement effects. They exhibit higher stability against moisture in an air environment, which benefits from the intrinsic structure with a layered arrangement of Pb–X polyhedron and Cs$^+$. Research of the fundamental structure–property correlation of CsPb$_2$X$_5$ could bring out the design inspiration of novel materials. Although CsPb$_2$X$_5$ has been shown to exhibit enhanced optical properties, problems regarding underlying mechanisms of the structural evolution and properties remain unclear. For example, 2D CsPb$_2$Br$_5$ has been previously synthesized, while 2D CsPb$_2$I$_4$ was only theoretically predicted, waiting to be validated experimentally. This provokes the exploration of more universal methods for the synthesis of 2D CsPb$_2$X$_5$.

For the synthesis of 2D perovskite-like analogue CsPb$_2$X$_5$, a wide variety of methods have been employed. The direct synthesis starts from the raw precursors, and the structures and properties of the resulting products are highly dependent upon the CsX/PbX$_3$ stoichiometric ratio and the thermodynamic conditions but still lacking general principles to follow. The post-synthesis, breaking up the three-dimensional (3D) metal halide perovskite network into low-dimensional perovskite-related networks, is an effective strategy, which has been proven by a variety of experimental results. For instance, the ligand-assisted excess PbBr$_2$ insertion or adding extra bromide source (such as NaBr) could transform CsPbBr$_3$ to Br-rich CsPb$_2$Br$_5$ with the chemical reaction of CsPbX$_3$ + PbX$_2$ → CsPb$_2$X$_5$; CsX stripping is also a promising approach by means of the ultrahigh solubility of CsX in polar solvents, following the pathway: CsPbX$_3$ → CsPb$_2$X$_5$ + CsX. However, the traditional synthesis methods usually require several raw precursors, follow complex chemical reaction steps, and produce CsPb$_2$X$_5$ accompanied by impurities and defects in the products. In particular, these methods require capping ligand mediations (such as oleic acid and oleyl amine) or multiple solvents (such as dimethylformamide and tetrahydrofuran) for different purposes, i.e., decreasing the surface energy and stabilizing the crystal structure. Here, we present a new synthesis process of CsPb$_2$X$_5$ under high pressure and thermal treatments via the direct-phase separation of CsPbX$_3$, which is distinguished from conventional methods.

Pressure, as a thermodynamic variable, provides an effective knob to synthesize novel materials, which cannot be achieved using traditional techniques. In combination with in situ characterization methods, high-pressure research could provide a better fundamental understanding of the chemical reaction
Figure 1. Structural evolution of CsPbI$_3$ upon heating at high pressure. (a) 2D diffraction images and (b) one-dimensional (1D) integrated XRD profiles at different temperatures. (c) XRD patterns of high P–T phases obtained by heating CsPbBr$_3$ and CsPbI$_3$ at high pressure in comparison to calculated XRD patterns (dot lines) using the tetragonal structure predicated theoretically (material project, mp-1238789). (d) Typical HRTEM image of the high P–T phase of CsPbI$_3$.

and crystal growth mechanisms.$^{34–37}$ Previous research has reported that the perovskite MgSiO$_3$$^{38}$ and its traditional low-pressure analogues (such as NaMgF$_3$$^{39}$ and MgGeO$_3$$^{40}$) could be dissociated into AB$_2$X$_4$ (P$\bar{2}$$_1$/c type) and BX (CsCl type) under high pressures, which have been reported in ABX$_3$ systems by following the transition sequence of perovskite $\rightarrow$ post-perovskite $\rightarrow$ U$\beta$S-type post-post-perovskite $\rightarrow$ P$\bar{2}$$_1$/c-type AB$_2$X$_4$. This provides an alternative method to synthesize 2D perovskite-like analogue CsPb-X$_4$ formed from 3D perovskite CsPbX$_3$ at high-pressure and high-temperature (P–T) conditions. In this work, we report the synthesis of 2D CsPbX$_4$ (X = Br and I) by the direct conversion of CsPbI$_3$ at high P–T conditions with the reaction of 2CsPbI$_3$ $\rightarrow$ CsPbBr$_3$ + CsX. CsPbI$_3$ is focused, because the synthesis using the traditional methods is rarely reported. Variations of structural and optical properties were systematically investigated using in situ synchrotron X-ray diffraction (XRD) and ultraviolet-visible (UV–vis) absorption spectroscopy. Newly obtained CsPbI$_3$, displays flexible optical properties while keeping the tetragonal structure stable up to 33.3 GPa. Note that both CsPbI$_3$ and CsPbBr$_3$ display a similar transformation into 2D CsPbX$_4$, indicating that the phase separation of CsPbX$_3$ (X = Br and I) is a general phenomenon at high P–T conditions. This work not only presents a general method for the synthesis of 2D perovskite derivatives at high P–T conditions, which is unachievable using traditional methods, but also provides deep insight into the formation mechanism.

At ambient conditions, $\delta$-CsPbI$_3$ is the stable phase and adopts an orthorhombic structure with space group Pnma and lattice constants of a = 10.4342(7) Å, b = 4.7905(3) Å, and c = 17.7761(1) Å.$^{31}$ The crystal structure of $\delta$-CsPbI$_3$ is built by double chains of edge-sharing [PbI$_6$]$^{10}$ octahedra separated by Cs$^+$ cations and transforms to a typical 3D perovskite structure featured with the corner-sharing [BX$_6$]$^{14}$ octahedra below 1 GPa and above 370 K.$^{42}$ In this work, the CsPbI$_3$ crystal was compressed up to around 8.7 GPa. XRD patterns show a phase transformation occurring at ~4 GPa from a $\delta$-CsPbI$_3$ phase to a high-pressure monoclinic structure (Figure S1 of the Supporting Information), consistent with previous reports.$^{35,46}$ Keeping the pressure at 8.7 GPa, the monoclinic CsPbI$_3$ sample was heated to investigate the structural evolution with the temperature using externally heated DACs. As shown in Figure 1, the high-pressure monoclinic phase is kept stable up to 638 K with the temperature increasing. Above 638 K, new diffraction peaks emerge with the disappearance of parent peaks, indicating a phase transition. The high P–T phase co-exists with the room-temperature (RT) monoclinic phase at temperatures from 644 to 652 K, and the high P–T phase was observed above 660 K with homogeneous diffraction rings (panels a and b of Figure 1). The sample was then cooled, and the high P–T phase can be quenched to room temperature. The pressure changes slightly from 8.7 to 6.7 GPa during heating and cooling processes. The high P–T phase is reserved during the pressure release (Figure S2 of the Supporting Information). The high P–T phase formed from CsPbI$_3$ cannot be assigned to the post-perovskite or any previously reported phase in ABX$_3$, such as CsGeI$_3$$^{45}$ and EuNbO$_3$.$^{28}$ Using the program Dicvol, most of the diffraction peaks can be well-indexed into a tetragonal phase with the space group I4/mcm. The feature reflections fit well into calculated XRD patterns of CsPb$_2$I$_4$ (Figure 1c), indicating the formation of CsPb$_2$I$_4$ by conversion of CsPbI$_3$ with the following process of 2CsPbI$_3$ $\rightarrow$ CsPb$_2$I$_4$ + CsI. The peaks at 19.1° together with some weak peaks can be attributed to CsI with a = 4.57 Å, consistent with previous reports.$^{46}$

The structural evolution at high P–T conditions is repeatable in CsPbI$_3$, and a similar process was observed in CsPbBr$_3$ upon heating up to 623 K at 8.3 GPa (Figure 1c and Figures S3 and S4 of the Supporting Information). CsPb$_2$Br$_3$ acts as an extension of the new approach under high P–T conditions, revealing that the formation of CsPb$_2$X$_3$ by phase separation of CsPbX$_3$ at high P–T conditions is reliable. Figure 1d and Figure S5 of the Supporting Information show the high-resolution transmission electron microscopy (HRTEM) images of the recovered sample. The interfringe distances of 0.32 and 0.35 nm could be indexed to the (220) and (114)
lattice planes of tetragonal CsPb₂I₅, respectively. The recovered sample with uniform surface morphology was demonstrated by scanning electron microscopy (SEM), and the homogeneous elemental distributions was quantified by energy-dispersive spectroscopy mapping (Figure S6 of the Supporting Information).

Figure 2. Crystal structure of CsPb₂I₅ at (a) 0 GPa and (b) 33.3 GPa. The ticks at the bottom indicate CsPb₂X₅ (red) and CsI (green) Bragg positions, respectively. (c) Crystal structural schematics of CsPb₂X₅.

Figure 3. In situ structural characterizations of CsPb₂I₅ under high pressures. (a) XRD patterns at selected pressures. The green arrow represents the recognizable peak of CsI. The dashed line is the pattern for the recovered sample from high P−T conditions. (b) Lattice parameters and (c) cell volume as a function of the pressure.
The structural variations of CsPb2I5 under high pressures were further investigated. Upon compression, all diffraction peaks shift to higher 2θ angles as a result of the lattice contraction. No new Bragg peaks can be observed (Figure 3a), implying that CsPb2I5 keeps the tetrahedral structure stable up to 33.3 GPa. The d-spacing decreases continuously with increasing pressure, as shown in Figure 2c. One layer of Cs cations is sandwiched between two layers of the Pb2I5 coordination polyhedron, wherein the Pb2I5 layers consist of Pb atoms coordinated with eight I anions, different from the perovskite structure with edge- or corner-sharing octahedra. In the Pb2I5 polyhedral layer, each Pb-I polyhedron is connected by faces and has two short bonds of 3.05Å, two bonds of 3.37 Å, and four long bonds of 3.54 Å, respectively.

The structural variations of CsPb2I5 under high pressures were fitted well to tetragonal CsPb2I5 (Figure 2c). The lattice parameters and cell volume of CsPb2I5 under high pressure are displayed in panels b and c of Figure 2c. The detailed absorption spectrum and bandgap change is quite monotonic with pressure releasing (Figure 4c). At ambient conditions, the sample was pale yellow. With pressure increasing, the colors of the sample gradually became red and then transformed into black at above 16 GPa. In addition, the main peaks of the optical absorption spectra decompressed from 36.9 GPa can be seen in Figures S11–S13 of the Supporting Information. Similar changes can also be traced from optical micrographs of CsPb2I5 during compression–decompression cycling in Figure 4c. At ambient conditions, the sample was pale yellow. With pressure increasing, the colors of the sample gradually became red and then transformed into black at above 16 GPa. In addition,
CsPb2I3 with the tetrahedral structure shows no PL emission at either high pressure or ambient conditions.

The tunability of the bandgap in the metal halide perovskites with a stable structure is important for optoelectronic applications. As shown in Figure 5a, we summarize the pressure-dependent bandgap of cesium lead halide perovskite and its derivatives, including CsPbBr3, CsPbBr5, δ-CsPbI5, α-CsPbI3, and newly reported CsPbI3. Generally, most of these materials exhibit an abrupt change of the optical bandgap accompanied by the crystal structural transitions (Figure 5a). Interestingly, the layered phase of CsPbI3 exhibits flexible bandgap tunability from 2.38 eV at ambient pressure to 1.68 eV at 18 GPa, while keeping the tetragonal structure stable upon compression. The superior bandgap tunability and highly stable structure endow CsPbI3 with promising applications in optoelectronics and pressure sensors. Considering promising possibilities, CsPbI3 could cooperate with CsPbI to fabricate high-quality composites.

On the basis of the XRD and previous research of CsPbI3, we tentatively show a P–T phase diagram in Figure 5b for synthesis of CsPbI3 by conversion of CsPbI. The formation of the α phase (high-temperature phase) and γ phase (thermodynamically metastable phase) can be transformed from the δ phase (low-temperature phase) of CsPbI3 when the applied pressure is below 2 GPa, whereas the high P–T conditions are required to synthesize CsPbI3 by conversion of high-pressure monoclinic CsPbI3. Once preserved to RT, tetragonal CsPbI3 can be retained, even after fully releasing pressure to ambient conditions.

It should be noted that the halide perovskite ABX3 can be a degradant at ambient conditions as a result of moisture and oxygen environmental sensitivity, following chemical equation: ABX3 → AX + BX2. 2D ABX3 has never been reported. Our work revealed for the first time that 2D CsPb2I3 can be obtained from CsPbI3 under high P–T conditions with the following pathway: 2CsPbI3 → CsPb2I3 + CsX. In comparison to the traditional synthesis methods of CsPb2I5 with several raw materials, multiple chemical reaction steps, injected impurities, and defects, the synthesis of CsPb2I3 at high P–T conditions is simple with a single chemical equation, and the product does not introduce new impurities.

Previous research reported that the perovskite ABX3 (such as NaMgF3) will be dissociated into AB2X5 (P21/c type) and AX (CsCl type) under high pressure. Theoretically, the calculation predicted the dissociations of ABX3 to AB2X5 as an endothermic reaction, which is related to the increases of bond lengths of A–X and B–X across the dissociations with increases of cation coordination numbers. Longer bonds lead to smaller optic phonon frequencies and larger vibrational entropy, which results in the lower Gibbs free energy. Likewise, CsPb2I3 has longer Pb–I and Cs–I bonds than CsPbI3 (please refer to the comparison of bond lengths between CsPbI3 and CsPb2I3 in Table S1 of the Supporting Information). The structures of cesium lead halide perovskites CsPbX3 are similar to NaMgF3 under ambient conditions. Thus, the formation mechanism of CsPb2I3 may be similar to that of NaMgF3, in which CsPb2I3 displays thermally structural stability with the lower Gibbs free energy than CsPbI3. The present work also reveals that the synthesis of 2D CsPb2I3 by conversion of perovskite CsPbX3 at high P–T conditions is a universal phenomenon with common characteristics that can be expanded to all perovskite/perovskite-related ABX3 systems. It also indicates that pure CsPb2I3 could be obtained by following the chemical reaction of CsPbI3 + PbI2 at high P–T conditions.

In summary, we demonstrate the synthesis of 2D CsPb2I3 (X = Br and I) by the direct conversion of CsPbX3 at high P–T conditions. Obtained tetragonal CsPb2I3 is quenchable at ambient conditions, having the lattice constants of a = b = 9.060(1) Å, c = 15.901(2) Å, and V = 1305.3(4) Å3. The structural and optical properties under high pressures were systematically investigated using XRD and absorption spectroscopy. CsPb2I3 exhibits flexible optical properties while keeping the tetragonal structure stable up to 33.3 GPa. Further experiments demonstrate that typical 3D CsPbBr3, with corner-shared [PbBr6]4− octahedrons displays a similar structural transformation into 2D CsPb2Br5, indicating that the synthesis of 2D CsPb2I3 by conversion of CsPbX3 at high P–T conditions is a universal phenomenon with common characteristics that can be expanded to more perovskite systems. This work not only presents a new strategy for the synthesis of the perovskite derivatives at high P–T conditions but also sheds light on the exploration of novel low-dimensional perovskite materials.

Figure 5. (a) Summary of the pressure-dependent bandgap of cesium lead halide perovskite and its derivatives. The color changes indicate structural phase transition. Data are from refs 43, 47, 50, and 51 and this work. (b) Experimental routes from the high-pressure phase of CsPbI3 to CsPb2I3 at high P–T conditions. The color shows different phases of CsPbI3, i.e., the α phase (indigo), γ phase (gray, a thermodynamically metastable phase), δ phase (orange), high-pressure phase of δ-CsPbI3 (yellow), and CsPb2I3 obtained in this work (blue).
Yufeng Liu — School of Materials and Engineering, Shanghai Institute of Technology, Shanghai 200235, People’s Republic of China; orcid.org/0000-0002-2733-7733

Sheng Jiang — Shanghai Synchrotron Radiation Facility, Shanghai Advanced Research Institute, Chinese Academy of Science, Shanghai 201204, People’s Republic of China

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcl.2c00116

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the financial support from the National Key Research and Development Program of China (Grant 2021YFB3702102), the National Natural Science Foundation of China (NSFC, Grants 11974033 and U2141240), and the Shanghai Natural Science Foundation (Grant 20ZR1455400). The XRD measurements were performed at the 4W2 HP-Station, Beijing Synchrotron Radiation Facility (BSRF), and beamline 15U1, Shanghai Synchrotron Radiation Facility (SSRF), which were supported by the Chinese Academy of Sciences (Grants KJCX2-SW-N03 and KJCX2-SW-N20).

REFERENCES


