High-pressure-induced comminution and recrystallization of CH₃NH₃PbBr₃ nanocrystals as large thin nanoplates

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<p>Please submit a plain text version of your cover letter here.</p> <p>If you are submitting a revision of your manuscript, please do not overwrite your original cover letter. There is an opportunity for you to provide your responses to the reviewers later; please do not add them here.</p>	<p>Sep 02, 2017 Editors Advanced Materials</p> <p>Dear editors,</p> <p>I would like to submit our paper "High Pressure-Induced Comminution and Recrystallization of CH₃NH₃PbBr₃ Nanocrystals as Large Thin Nanoplates" by T.T. Yin et al., for publication in Advanced Materials, as an original article.</p> <p>High pressure (up to tens of gigapascals), as a clean and powerful tool, can effectively alter the crystal structures (J. Am. Chem. Soc. 137, 11144-11149, 2015; Angew. Chem. Int. Ed. 55, 6540-6544, 2016), finely tune the electronic structures (Energy Environ Sci 10, 509-515, 2017; J. Am. Chem. Soc. 139, 4330-4333, 2017), significantly increase conductivity (ACS Cent Sci. 2, 201-209, 2016), and modify the lifetime of carriers (Proc. Natl. Acad. Sci. U.S.A 113, 8910-8915, 2016) in hybrid perovskite ABX₃ (A is a cation: Cs⁺, CH₃NH₃⁺ (MA⁺) and CH(NH₂)₂⁺ (FA⁺); B is a metal cation: Pb²⁺, Sn²⁺; X is a halide anion: Cl⁻, Br⁻, I⁻) single crystals. However, such pressure-induced modifications on crystal structures and functional properties in most bulk perovskites will disappear after release of pressure. Only most recently, a few high-pressure work reports irreversibility in bulk perovskite materials (Adv. Mater., 28, 8663-8668, 2016; Adv. Funct. Mater., 27, 1604208, 2017; Adv. Mater., 29, 1606666, 2017). On the other hand, for conventional nanocrystals (Ag/Au, CdSe/PbS ...), high pressure can drive the direct sintering of nanoparticle assemblies. The formed nanoparticle architectures possess new physical/chemical properties in ambient environments (Nat. Commun. 5, 4179, 2014; Sci. Adv. 3, e1602916, 2017).</p> <p>In this paper, beyond conventional nanocrystals, we experimentally observe for the first time high-pressure-induced comminution and recrystallization of organic-inorganic hybrid perovskite nanocrystals into highly luminescent nanoplates with a shorter carrier lifetime. Such anomalous/novel pressure response is attributed to the unique structural nature of hybrid perovskites under high pressure: during the drastic structural transformation, some crystal plane fully occupied by organic molecules possesses a higher surface energy, triggering the comminution along such crystal plane. After release of the pressure, the formed variants, i.e., perovskite nanoplates, are retained and exhibit simultaneous photoluminescence emission enhancing and carrier lifetime shortening, showing potential applications for nanolasers and light-emitting devices.</p>

	<p>Highlights of this work:</p> <p>First high-pressure study on organic-inorganic hybrid perovskite nanocrystals;</p> <p>New mechanism of the morphology evolution under high pressure;</p> <p>Advanced optical properties are retained after releasing of pressure.</p> <p>We deeply appreciate your kind consideration and look forward to your constructive comments about this manuscript.</p> <p>Nominated reviewers:</p> <p>1.Prof. Hongyou Fan (hfan@sandia.gov), Sandia National Laboratories, USA. Research field: High pressure studies on metallic nanoparticles and conventional semiconductors</p> <p>2.Prof. Guichuan Xing (gcxing@umac.mo), University of Macau, Macau, China. Research field: Nonlinear optical properties and ultrafast carrier dynamics in perovskite materials)</p> <p>3.Prof. Su-Huai Wei (suhuaiwei@csrc.ac.cn), Beijing Computational Science Research Center, China. Research field: Theoretical calculations on semiconductors and perovskites</p> <p>4.Prof. Changqing Jin (Jin@iphy.ac.cn), Institute of Physics, Chinese Academy of Sciences, China Research field: High pressure physics</p> <p>5.Prof. Michael Graetzel (michael.graetzel@epfl.ch), Ecole Polytechnique Fédérale de Lausanne (EPFL), Swiss. Research field: Perovskites-based solar cell</p> <p>6.Prof. Ivan Scheblykin (ivan.scheblykin@chemphys.lu.se), Lund university, Sweden Research field: Spectroscopy studies on perovskites</p> <p>7.Prof. Pavel Troshin (p.troshin@skoltech.ru), Skolkovo Institute of Science and Technology, Russia Research field: Perovskite materials</p> <p>8.Prof. Lain-Jong Li (lance.li@kaust.edu.sa), King Abdullah University, Saudi Arabia Research field: Spectroscopy studies on perovskites and TMDs</p> <p>Yours sincerely,</p> <p>Ze Xiang Shen, Professor</p> <p>Program Chair (Sustainable Earth), Interdisciplinary Graduate School Co-Director, Centre for Disruptive Photonic Technologies. Division of Physics and Applied Physics, School of Physical & Mathematical Sciences Nanyang Technological University, Office: SPMS-PAP-03-01, 21 Nanyang Link, Singapore 637371 Tel: (65) 6316-8855 GMT+8h Fax: (65) 6515-8229 Email: zexiang@ntu.edu.sg Web: http://www1.spms.ntu.edu.sg/~zexiang</p>
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Abstract:	<p>High pressure can drive the direct sintering of nanoparticle assemblies for Ag/Au, CdSe/PbS nanocrystals. Here, instead of direct sintering for the conventional nanocrystals, we experimentally observe for the first time high-pressure-induced comminution and recrystallization of organic-inorganic hybrid perovskite nanocrystals into highly luminescent nanoplates with a shorter carrier lifetime. Such novel pressure response is attributed to the unique structural nature of hybrid perovskites under high pressure: during the drastic cubic-orthorhombic structural transformation at ~2 GPa, (301) crystal plane fully occupied by organic molecules possesses a higher surface energy, triggering the comminution of nanocrystals into nanoslices along such crystal plane. Beyond bulk perovskites, in which pressure-induced modifications on crystal structures and functional properties will disappear after pressure release, our pressure-formed variants, i.e., large (~100 nm) and thin (<10 nm) perovskite nanoplates, are retained and exhibit simultaneous photoluminescence emission enhancing (a 15-fold enhancement in the photoluminescence) and carrier lifetime shortening (from $\sim 18.3 \pm 0.8$ ns to $\sim 7.6 \pm 0.5$ ns) after releasing of pressure from 11 GPa. This pressure-induced comminution of hybrid perovskite NCs, and subsequent an amorphization-recrystallization treatment offer the possibilities of engineering the advanced hybrid perovskites with specific properties.</p>

High Pressure-Induced Comminution and Recrystallization of CH₃NH₃PbBr₃ Nanocrystals as Large Thin Nanoplates

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Abstract

High pressure can drive the direct sintering of nanoparticle assemblies for Ag/Au, CdSe/PbS nanocrystals. Here, instead of direct sintering for the conventional nanocrystals, we experimentally observe for the first time high-pressure-induced comminution and recrystallization of organic-inorganic hybrid perovskite nanocrystals into highly luminescent nanoplates with a shorter carrier lifetime. Such novel pressure response is attributed to the unique structural nature of hybrid perovskites under high pressure: during the drastic cubic-orthorhombic structural transformation at ~ 2 GPa, (301) crystal plane fully occupied by organic molecules possesses a higher surface energy, triggering the comminution of nanocrystals into nanoslices along such crystal plane. Beyond bulk perovskites, in which pressure-induced modifications on crystal structures and functional properties will disappear after pressure release, our pressure-formed variants, *i.e.*, large (~ 100 nm) and thin (< 10 nm) perovskite nanoplates, are retained and exhibit simultaneous photoluminescence emission enhancing (a 15-fold enhancement in the photoluminescence) and carrier lifetime shortening (from $\sim 18.3 \pm 0.8$ ns to $\sim 7.6 \pm 0.5$ ns) after releasing of pressure from 11 GPa. This pressure-induced comminution of hybrid perovskite NCs, and subsequent an amorphization-recrystallization treatment offer the possibilities of engineering the advanced hybrid perovskites with specific properties.

Introduction

Under sufficient pressure, the surface states^[1], crystallography^[2], electronic properties^[3] and carrier dynamics^[4] of materials alter significantly. In particular, the compression of appreciable hybrid perovskite single crystals has been studied intensively to finely tune the crystal structures (phase transitions) and to realize new properties (electronics and dynamics) via lattice compression. Wang *et al.*^[5] described pressure-induced phase transformations and anomalous band gap evolution in methylammonium (MA) lead bromide $\text{CH}_3\text{NH}_3\text{PbBr}_3$, while Karunadasa *et al.* and Zhou *et al.* examined electronic and conductive variants of hybrid 3D perovskites^[6] and Cu-Cl 2D perovskites^[7]. For example, high pressure-induced a semiconductor-to-metal transition in MAPbI_3 with the bandgap continuously decreasing from 1.6 to ca. 0 eV and the onset of superconductivity^[8]. Katrusiak *et al.*^[9] systematically studied high-pressure effects on bond length contraction and bond angle bending in three typical hybrid perovskites ($\text{MAPbCl}_3/\text{Br}_3/\text{I}_3$). More recently, Kong *et al.*^[4] achieved unprecedented carrier-lifetime prolongations of 70% to $\sim 100\%$ in $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystals by applying ~ 0.3 GPa. However, structure-property correlations under compression, including changes in symmetry, bandgap and carrier lifetime remain to be completely described, but are possibly linked to the PbX_6 octahedral tilting, organic cation disorder-ordering or the defects arising from amorphization^[4-5, 6c]. Moreover, in large crystals the physical and chemical properties are usually restored after pressure release.

Nanocrystals (NCs) respond specifically to pressure with respect to phase progression^[10], coherent crystal domain size^[11], particle agglomeration^[12] and morphology^[13], accompanied by physical and chemical property modification. For example, high pressure can induce distinct textural coalescence of metallic Au/Ag NCs along with tuning the corresponding

plasmonic resonance^[14]; (meta)stable phases in conventional semiconductors including CdSe^[15] and PbS/Pt^[15a, 16], and alternation in the carrier dynamics in CdTe NCs^[17] and CsPbBr₃ perovskite nanocube superlattices^[18].

In this work, we discover a novel high-pressure response of organo-inorganic hybrid perovskite NCs, *i.e.*, the pressure-driven a comminution MAPbBr₃ NCs into nanoslices during a drastic phase transition, accompanying with ultimate recrystallization as large thin nanoplates (NPs) after amorphization and recrystallization. These investigations are employed a diamond anvil cell (DAC) to compress ~10 nm MAPbBr₃ NCs (space group: $Pm\bar{3}m$). Based on *in situ* synchrotron X-ray diffraction (XRD) results, a series of transmission electron microscopy (TEM) images and *Ab initio* calculations, we reveal the mechanism is associated with the pressure-induced phase transitions and amorphization with pressure increases. The optical measurements before and after pressurization indicate that the high-pressure-treated product shows improved optoelectronic properties as compared to original sample, proving advantageous for nanolaser and light-emitting diode applications^[19]. Our discovery reveals improved structural stability with enhanced optical properties for organic-inorganic hybrid perovskite nanocrystals via a pressure-induced comminution and recrystallization process.

Results and discussions

The MAPbBr₃ NCs synthesized by ligand-assisted re-precipitation (see Methods section) have an average diameter of ~10 nm (Figure 1a) and are highly crystalline (Figure 1b). The DAC diamond flat was loaded by direct drop-casting of NCs dissolved in toluene followed by solvent evaporation (Figure 1c). *In-situ* high-pressure synchrotron powder X-ray diffraction (XRD)

monitored lattice evolution under compression (up to ~11 GPa) and release. At ambient pressure the MAPbBr₃ is cubic $Pm\bar{3}m$ ($a = 5.8725$ Å). From 0.11 - 0.99 GPa, the Bragg reflections progressively shift to higher diffraction angles (unit cell volume reduction) as expected. At 0.99 GPa, two additional weak reflections appear at $2\theta \sim 7.6^\circ$ and 9.0° indicating a pressure-induced phase transition. Pawley fitting is consistent with the $Im\bar{3}$ ($a = 11.5600$ Å) polymorph with a doubled cell edge compared to the $Pm\bar{3}m$ phase. As pressure rose to ~2.41 GPa the reflection near 9.8° split indicative of the orthorhombic ($Pnma$, $a = 7.978$ Å, $b = 11.4507$ Å, $c = 8.001$ Å) modification. Above ~4.06 GPa a broad background (centered at $\sim 10.5^\circ$) appeared, and the intensities of all diffraction reflections decreased due to amorphization, while the $(001)_{\text{cubic}}$ peaks remain up to ~11 GPa, indicative of partially periodic atomic order. Upon decompression, the amorphous MAPbBr₃ returned to the cubic $Pm\bar{3}m$ phase with slightly lattice contraction ($a = 5.8740$ Å).

The XRD results are consistent with $Pm\bar{3}m$ (cubic) $\rightarrow Im\bar{3}$ (cubic) $\rightarrow Pnma$ (orthorhombic) transitions and partial amorphization beyond ~4.0 GPa, as reported for large MAPbBr₃ crystals^[5, 20], and manifest the evolution of low-frequency Raman spectra (Figure S1). The corresponding atomic models are shown in Figure 1e and the fitted lattice parameters are presented in Figure S2. In the pristine perovskite ($Pm\bar{3}m$), PbBr₆ octahedral topology creates a regular cubic network, while the MA cation (with C_{3v} molecular symmetry) is disordered over 12 $\langle 110 \rangle$ directions to satisfy O_h symmetry^[21]. Within the octahedra, the Pb-Br bond shortens under pressure (Figure S3a), and the Pb-Br-Pb bridging angle progressively becomes more acute beyond 0.99 GPa (Figure S3b). The Br atoms are displaced from the special Wyckoff $3c$ sites to occupy $24g$ sites consistent with PbBr₆ octahedra with $a^+a^+a^+$ Glaser tiltings of equal magnitude about all the pseudocubic axes^[22]. The volume reduction of PbBr₆ octahedron (Figure S4a) and MABr₁₂ polyhedron (Figure S4b) along with the tilting of PbBr₆

(table S1) induce the $Im\bar{3}$ transition. By further increasing the pressure, the relatively rigid $PbBr_6$ octahedra adopt $a^+b^-b^-$ tilting system ($Pnma$) (Table S1)^[20] accompanied by orientational ordering of MA cations due to hydrogen-bonding interactions^[23]. As commonly observed in perovskites, the contraction of unit cell volume (Figure S5) and tilting of $PbBr_6$ octahedra (Table S1) are the principal driving force for the phase transitions under compression, demonstrating the relative ease of MA cation compressibility. The phase transitions are also evidenced by the piezochromism in $MAPbBr_3$ NCs (Figure 1f).

To visualize the high-pressure-induced comminution and reconstruction of $MAPbBr_3$, the evolution of NC morphology was examined by transmission electron microscopy (TEM) of the retrieved $MAPbBr_3$ products from the DAC, after pressure released from 0.75 GPa, 2.23 GPa, 6.5 GPa and 11 GPa respectively (Figure 2). After pressure release from ~0.75 GPa, the NCs deform and agglomerate to form clusters (Figure 2a,b), but after pressure treatment at ~2.23 GPa (Figure 2c,d) comminution leads to nanoslices with ribbon-like projections appearing within rectangular boundaries. The selected area electron diffraction (SAED) pattern (inset) and phase contrast TEM image demonstrates the nanoslices are single crystals. In ambient condition, the lattice fringes ($\sim 0.26 \pm 0.02$ nm) agree well with (210) d-spacing in cubic phase and confirm comminution on the corresponding (301) lattice planes in orthorhombic phase. From ~6.5 GPa release, imperfect nanoplates with evident extended defects are recognized (Figure 2e,f), while large homogeneous crystals appear after ~11 GPa release (Figure 2g,h). Taken together, microscopy suggests that pressure induces comminution and recrystallization of $MAPbBr_3$ NCs via (Figure 2i): (1) deformation and division of the NCs into nanoslices that expose fresh (301) interfaces during the cubic-orthorhombic transformation to create 1D ribbons (Figure 2d); then (2) the detachment of nanoslices with capping ligands via amorphization, recrystallize (3) as single-crystal NPs (Figure 2h) upon decompression.

To understand the structural mechanism underlying NC comminution under pressure, Figure 3a shows the atomic structural relationship between the cubic and orthorhombic phases. The $(301)_{\text{ortho}} \equiv (210)_{\text{cubic}}$, are nearly co-incident lattices ($d \sim 0.26 \pm 0.02$ nm) (Figure 2d). The PbBr_6 octahedra in the orthorhombic polymorph are tilted in the same (in-plane tilt a^+) and opposite (anti-plane tilt b^- and c^-) sense^[22], and the Pb and Br atoms move out of the $(210)_{\text{cubic}}$ planes. Finally, the $(301)_{\text{ortho}}$ crystal planes are fully occupied by an ordered arrangement of MA cations. The complex in-plane and out-of-plane tilting of PbBr_6 octahedra (Table S1) accompanied with the increase of broken Pb-Br bonds, drives the MAPbBr_3 NCs to comminute spontaneously along $(301)_{\text{ortho}}$ under compression. First-principles calculations are consistent with the experimental observations, as the $(210)_{\text{cubic}}$ have a cleavage energy of $20.6 \text{ meV}/\text{\AA}^2$ and a higher cleavage energy of $117 \text{ meV}/\text{\AA}^2$ in the orthorhombic phase at 2.5 GPa, indicating such crystal planes are more easily cleave under pressure compared to other low-index planes. Starting from the optimized cubic structure of MAPbBr_3 , five low-index planes of $(010)_{\text{cubic}}$, $(110)_{\text{cubic}}$, $(111)_{\text{cubic}}$, $(210)_{\text{cubic}}$ and $(301)_{\text{ortho}}$ were considered here for the cleavage energy calculations based on the TEM results by using slab models^[24], in which a set of infinite periodic layers separated by ($>15 \text{ \AA}$) to create a synthetic surface (Figure S6). Each low-index plane consists of a pair of symmetrically terminated slabs with four surfaces exposed to vacuum. The comminution energy of each low-index plane can be obtained as:

$$\gamma = \frac{E_{\text{slab}(A)} + E_{\text{slab}(B)} - nE_{\text{bulk}}}{4A}$$

where γ is the cleavage energy; E_{slab} is the total free energy of the slabs with two complementary terminations (A and B) for each surface; n is the total surface layer number in each low-index plane and E_{bulk} is the total energy of the bulk MAPbBr_3 crystal.

In this manner, (210)_{cubic} crystal planes were constructed with stoichiometric MABr-termination and PbBr₂-termination without polarization (Figure 3b). The calculated cleavage energy for other three low-index surfaces: 24.7 meV/Å² for (010)_{cubic} surfaces, 20.8 meV/Å² for (110)_{cubic} surfaces, and 29.8 meV/Å² for (111)_{cubic} surfaces, which manifests with our crystal morphology in Figure 1b. As a comparison, in the orthorhombic system at 2.5 GPa, (301)_{ortho} shows a higher cleavage energy of ~117 meV/Å², demonstrating this crystal planes more easily cleave along the (301)_{ortho} under pressure.

Steady-state and time-resolved photoluminescence (TRPL) spectroscopy evaluated the evolution of optical behaviors associated with pressure-induced morphological changes and polymorphic transitions (Figure 4a, c). A red shift (from 533 to 546 nm) of the PL emission peak at < ~1 GPa in the *Pm* $\bar{3}$ *m* polymorph, is followed by a continuous blue shift in the *Im* $\bar{3}$ (from 546 to 525 nm) and *Pnma* polymorphs (from 522 to 502 nm) (the circles in Figure 4b). Above ~4.0 GPa, MAPbBr₃ amorphizes with extremely broad and weak emission (Figure S7). The band gap narrowing in *Pm* $\bar{3}$ *m* could be ascribed to Pb-Br bond length contraction (Figure S3a), leading to the enhancement of ~60 times in PL emission intensity^[6a, 25] (Figure 4b). Further compression decreases the Pb-Br-Pb bond angle (Figure S3b) along with reduced Pb *s* and Br *p* orbital coupling^[4, 25], resulting in band gap widening. Discontinuities in PL intensity at ~0.8 GPa and ~2 GPa arise from nonradiative recombination introduced by octahedral tilting and the onset of the pressure-induced amorphization^[5] as well as the presence of surface defects during comminution.

Phase transitions and morphological changes of the NCs inevitably modifies carrier dynamics that can be analyzed through TRPL spectral fitting. A biexponential treatment ($I_{\text{PL}}(t) = I_{\text{int}} [A_{\text{slow}} \exp(-t/\tau_{\text{slow}}) + A_{\text{fast}} \exp(-t/\tau_{\text{fast}}) + I_0]$) can be used to extract the mean carrier time ($\langle\tau\rangle$)

$= [A_{\text{slow}} \tau_{\text{slow}}^2 / (A_{\text{slow}} \tau_{\text{slow}} + A_{\text{fast}} \tau_{\text{fast}})] + [A_{\text{fast}} \tau_{\text{fast}}^2 / (A_{\text{slow}} \tau_{\text{slow}} + A_{\text{fast}} \tau_{\text{fast}})]$ (Figure 4c), where τ_{slow} and τ_{fast} are assigned to a bulk component and a surface component respectively^[4, 26] (see more fitting details in Figure S8). The mean carrier lifetime is prolonged in $Pm\bar{3}m$ under mild compression due to lattice shrinkage^[18] and surface reconstruction^[27] with a dramatical change of the fast and slow components (Figure S8b,c). Upon further compression, lifetimes shorten as defects arising from the phase transition, and the larger band gap (Figure 4b) creates both the surface and bulk states relatively deeper, leading to more nonradiative recombination^[4]. At the critical pressure of ~2 GPa lifetimes are minimum to $\sim 7.8 \pm 0.6$ ns due to the creation of numerous surface states introduced by comminution where the fast and slow component become comparable (Figure S8c). Amorphization leads to broadband emission from self-trapped states induced by a loss of periodicity, insertion of interfacial faults, and a higher concentration of grain boundaries during pressure (Figure S7).

After a single pressure cycle, new optical properties appear for MAPbBr₃ NCs after a single pressure cycle. The PL of the large NPs is blue-shifted ~5 nm with an ~15-time enhancement in the emission (Figure 5a), due to a strengthened quantum confinement arising from pressure-induced comminution of the NCs into nanoslices. The mean carrier lifetime shortens from $\sim 18.3 \pm 0.8$ ns to $\sim 7.6 \pm 0.5$ ns (Figure 5b) as more surface states exist in the perovskite NPs (Figure 2h). The pressure-produced highly luminescent hybrid perovskite NPs with a shorter carrier lifetime are potentially applicable to nanolasers and light-emitting diodes.

Conclusions

In summary, it is demonstrated for the first time that pressure can regulate the comminution and recrystallization of MAPbBr₃ NCs. The dissociation of the NCs is driven by PbBr₆

1 octahedral tilting and MA cation re-orientation accompanying transformation to the
2 orthorhombic polymorph. This growth mechanism differs from that in metallic/organic
3 semiconductor nanoparticles (Au, Ag, CdSe, PbS)^[14a, 15] and CsPbBr₃ perovskite QDs^[18], *i.e.*,
4 pressure-driven large single-crystal formation from direct attachment and sintering of those
5 nanoparticles. The application of external pressure is a simple route for engineering perovskite
6 nanocrystals with prescribed quantum properties, and may prove useful for fabricating of
7 micro-/nano-electronic devices.
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19 **Methods**

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24 **MAPbBr₃ NCs synthesis.** MAPbBr₃ NCs were synthesized by the ligand-assisted re-
25 precipitation method^[28], where 5-aminovaleric acid was first converted into its ammonium salt
26 (Br⁻NH₃⁺-(C₂H₂)₄-COOH) with a slight excess of hydrobromic acid (HBr). Subsequently, 0.5
27 ml of PbBr₂ (40 mM in DMF), 0.5 ml of MABr (40 mM in DMF), 95 μL of oleic acid and 3
28 μL of Br⁻NH₃⁺-(C₂H₂)₄-COOH were homogenously mixed and quickly injected into 10 ml of
29 toluene under vigorous stirring at room temperature (RT). The resulting solution was
30 centrifuged at 4000 rpm for 10 minutes and the precipitate collected and centrifuged again after
31 redispersion in toluene.
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46 **Diamond anvil cell.** Two identical diamond anvils with a culet of 500 μm were employed to
47 generate pressure. A stainless-steel gasket was pre-indented to 50 μm with a drilled hole 200
48 μm in diameter serving as the sample chamber. The MAPbBr₃ NCs and a small ruby ball were
49 loaded together into the diamond anvil cell (DAC). The pressure was calibrated using the
50 pressure-dependent ruby fluorescent technique.
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***In situ* HP-XRD** was carried out on the B1 station at the Cornell High Energy Synchrotron Source (CHESS) with monochromatic X-ray radiation ($\lambda = 0.485946 \text{ \AA}$ (25.514 KeV))^[3c]. Experimental fitting of the X-ray synchrotron data was carried out using TOPAS 3 employing the fundamental parameter approach.

***In situ* HP optical measurements** used silicone oil as the pressure transmitting fluid. (1) Steady-state absorption/PL and Raman spectra were collected during compression and release under the WITec alpha 300RAS microscope. For the absorption measurements, a halogen lamp (15 V, 150 W, 3100 K) was chosen as the white light source. For the PL measurements, a linearly polarized CW solid laser (457 nm, 30 μ W) was used for excitation, while a linearly polarized CW He-Ne gas laser (633 nm, 8 mW) was chosen for Raman measurement. A long working distance 20 $\times$ microscope objective (spot size $\sim 2 \text{ }\mu\text{m}$) focused light on the sample. Both the absorption and PL spectra were dispersed by a 150 groove/mm diffraction grating (0.5 nm resolution), while a 1800 groove/mm diffraction grating (1.3 cm^{-1} resolution) was chosen for the backscattered Raman signal collection. All optical signals are detected by a thermoelectric cooled Andor CCD detector. (2) For time-resolved PL measurements, the 400 nm excitation pulses were generated via second harmonic generation (with a beta barium borate crystal) of the 800 nm output from a Coherent Libra regenerative amplifier (50 fs, 1 kHz) seeded by a Coherent Vitesse oscillator (50 fs, 80 MHz). The 400 nm laser then entered a 650 nm short pass filter to remove residual 800 nm photons. This beam is directed into a Nikon microscope and focused onto the sample (mounted in the diamond anvil cell) using a 10 $\times$ objective lens. The laser diameter on the sample was $\sim 100 \text{ }\mu\text{m}$. The backscattered emission was collected using the sample objective via a 410 nm long pass filter to remove 400 nm excitation photons. The filtered emission is then directed into a monochromator (Acton,

Spectra Pro 2300) followed by an Optronis OptoscopeTM streak camera system to obtain the PL kinetics. The ultimate resolution of this system at the fastest scan speed is ~10 ps.

Microscope measurements were obtained from NCs deposited on holey carbon copper grids for transmission electron microscopy (TEM) using a JEOL JEM2100F instrument. Samples were analyzed after orientation with a double tilting holder and the selected area electron diffraction (SAD) patterns recorded. High-resolution phase contrast images were collected using an objective aperture of 20 mm, corresponding to a nominal point-to-point resolution of 0.17 nm.

Ab initio calculations were performed using the projector-augmented wave (PAW)^[29] method as implemented in the Vienna *Ab initio* Simulation Package (VASP)^[30]. The exchange correlation potential described by the Perdew, Burke and Ernzerhof (PBE) function was used within the generalized gradient approximation (GGA)^[31]. The energy convergence for the relaxation was chosen to be less than 10⁻⁵ eV/Å. Taking account of nonlocal van der Waals interactions, the newly developed vdW density functional (vdW-DF2) was used in this study^[32]. For the bulk phase, the Brillouin zone was sampled by a 6×6×6 k-point mesh using the Monkhorst-Pack (MP) method. For the slab models, a 4×4×2 MP k-point mesh was adopted. Each slab consisted of two symmetric terminations to avoid spurious dipole-dipole interactions between periodic slabs. In addition, only charge-balanced stoichiometric slabs were considered by adjusting the number of surface atoms while maintaining the symmetry constraint. For each of the five surfaces, ten possible terminations were constructed as follows: MABr- and PbBr₂- terminated (001)_{cubic} surfaces; Br₂- and MAPbBr- terminated (110)_{cubic} surfaces; MABr- and PbBr₂- terminated (210)_{cubic} surfaces; Pb- and MABr₃-terminated (111)_{cubic} surfaces, and MA- and PbBr₃-terminated (301)_{ortho} surfaces. Unlike the (100)_{cubic} and (210)_{cubic} surface with two

non-polar MABr- and PbBr₂- terminations, MAPbBr₃ (110)_{cubic}, (111)_{cubic}, and (301)_{ortho} surfaces with the stoichiometric terminations will give rise to a monotonic raised microscopic electric field, which is compensated through an anomalous filling of the surface electronic states. Finally, the cleavage energy (γ) of each surface was obtained as:

$$\gamma = \frac{E_{slab(A)} + E_{slab(B)} - nE_{bulk}}{4A}$$

where E_{slab} is the total free energy of the slabs with two complementary terminations (A and B) for each surface; and E_{bulk} is the total energy of the bulk MAPbBr₃ crystal.

Supplementary Information

Supporting Information is available from the Wiley Online Library or from the author.

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Author contributions

T.T.Y, J.X.Y and Z.X.S conceived the idea. T.T.Y conducted all the high-pressure steady-state optical measurements. J.X.Y (Dr.) performed the calculations.

Y.N.F (Dr.) and T.J. White (Prof.) performed all the TEM measurements.

K.T.M (Dr.) prepared the samples.

W.K.C. (Mr.) and T. C. Sum (Prof.) performed the time-resolved PL measurements.

S.J.J. and J.Y. Fang (Prof.) performed the high pressure XRD measurements.

X.L.L is a DAC expert and supervised the sample loading into DAC.

JLK provided the computation resource.

T.T.Y, Y.N.F, J.X.Y, Z.X.S and T.J. White analyzed the data and wrote the manuscript.

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Figures.

Figure 1. Pressure-induced phase transition and structural distortion. a) A typical LR-TEM image of MAPbBr₃ perovskite NCs with average diameter of ~10 nm. b) Plan-view HR-TEM image taken along [111] zone axis with the FFT pattern (inset) showing single-crystalline nature of the NCs. c) Overall schematic of the diamond-anvil cell (DAC) for high-pressure measurements and the zoomed-in image of DAC showing the model of initial MAPbBr₃ NCs. (MA model is simplified.) d) The integrated spectra from HP-XRD images at various pressures. e) The crystal structures in three phases, demonstrating PbBr₆ octahedra tilting and MA cations ordering during phase transformation. f) Optical micrographs of the piezochromic phenomenon during phase transition.

Figure 2. Pressure-induced comminution and recrystallization of perovskite NCs. (Left column)

A series of LR-TEM images of high-pressure-treated products, correlated to different growth stages of MAPbBr₃ NCs. (Right column) A series of HR-TEM images of the corresponding products and FFT patterns from selected sample regions (inset). i) Schematic of MAPbBr₃ NCs comminution and recrystallization under high pressure: ① Pressure-induced deformation and

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comminution of NCs into nanoslices along (301) planes in orthorhombic phase at the pressure of 2 GPa. ② Sintering and amorphization of nanoslices above 4 GPa ③ recrystallization (upon pressure release from 11 GPa) of nanoslices into large thin nanoplates along with interface relaxation.

Figure 3. Understanding of pressure-induced comminution from atomic-level. a) During the cubic to orthorhombic phase transformation, the PbBr_6 octahedra tilt along a^+b^- system. Red arrows represent the rotation directions. MA molecules are filled between (301) planes with ordered configuration, corresponding to (210) planes in cubic phase. b) The calculated $(210)_{\text{cubic}}$ and $(301)_{\text{ortho}}$ surface slab models.

Figure 4. Structure-property correlation of MAPbBr₃ NCs during high pressure-induced phase transition and comminution. a) The steady-state photoluminescence (PL) and absorption measurement of NCs before amorphization. b) The peak position and relative intensity of NCs during compression. c) Time-resolved PL (TRPL) measurement of NCs before amorphization and the mean carrier lifetime under compression. The colorful shallows represent three phases: *Pm* $\bar{3}$ *m* cubic, *Im* $\bar{3}$ cubic and *Pnma* orthorhombic phase.

Figure 5. Comparison of optical properties between the original MAPbBr₃ NCs and the pressure-synthesized MAPbBr₃ NPs. a,b) Steady-state PL and absorption spectra and TRPL kinetics before (grey) and after (red) compression with pressure up to 11 GPa.

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