





Pressure engineering of photovoltaic perovskites

Gang Liu^{1,*}, Lingping Kong^{1,*}, Wenge Yang^{1,*}, Ho-kwang Mao^{1,2}

¹ Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, China ² Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA 718-2019

As the driving force for technological innovations in the field of photovoltaic applications, metal halide perovskites have been extensively studied and significant research progress has been made in the last few years. Of particular interest is that with the addition of the pressure dimension, the development of the investigations has contributed significantly to the reliable detection of structure–property relationships. Furthermore, recent discoveries based on new perovskite materials and new characterizations have led to resurgence in studying not only the pressure-tailored physical properties but also the pressure-driven novel functionality, including the ambient performance after removing applied pressure. We will discuss the manipulation, modification, and improvement in photovoltaic perovskites by pressure engineering, which is crucial to achieve the desired characteristics for the next generation of material-by-design, as well as various applications.

Introduction and background

Renewable and clean energy sources have attracted significant attention from governments, scientific institutions, and universities, as well as commercial and industrial companies, all around the world. For example, the USA's SunShot Initiative Photovoltaics (PVs) project requires a levelized cost-of-energy (LCOE) of only \$0.03/kWh by 2030 [1]. It is imperative that inherently low-cost processes and earth-abundant materials are used in future PVs to realize this goal. In this context, solutionprocessed thin-film perovskite solar cells (PSCs) based on ABX₃ $(A = Cs, CH_3NH_3 (MA), HC(NH_2)_2 (FA); B = Pb, Sn; X = Cl, Br, I)$ halide perovskites (HPs) offer tremendous potential in meeting that goal [2–15]. While the field of PSCs has progressed in leaps and bounds, several challenges need to be addressed before PSCs can reach their full potential. The most critical and difficult among them are: (i) achieving both excellent environmental stability and outstanding photovoltaics performance of HPs from a practical viewpoint and (ii) obtaining a comprehensive understanding of the structure-properties relationship of HPs from a fundamental scientific viewpoint.

Currently, perovskite-based single-junction solar cells have achieved power conversion efficiency (PCE) of 23% [16]. However, further developments of perovskites seemingly suffer from a dilemma between high performance and instability issues [17]. HPs with the general formula ABX₃ have a perovskite structure, but the most studied HP for PSCs, MAPbI₃, degrades in a humid environment, where H₂O molecules displace the MA⁺ cations, resulting in the formation of hydrated intermediatecontaining isolated PbI_6^{4-} octahedra. While the major covalent character of the Pb-I bond promotes carrier transport, the minor ionic character renders the Pb-I bond weak and susceptible to attack by H₂O. To circumvent this dichotomy, other chemical variants or altered dimensionality perovskites (beyond 3D) are urgently needed for stable, long-term PV and optoelectronic applications. Two-dimensional (2D) hybrid perovskites with organic interlayers and inorganic sheets are reminiscent of a natural multi-quantum-well structure. These 2D hybrid perovskites offer significantly improved stability to various environmental triggers due to their inorganic networks confining the carriers and mobile ions [18-23]. Tsai et al. synthesized 2D Ruddlesden-Popper perovskites, and achieved a PCE of 12.52% in encapsulated solar cells, without any degradation over 2250 h under AM1.5G illumination or 65% relative humidity [18]. Based on

^{*} Corresponding authors

E-mail addresses: Liu, G. (liugang@hpstar.ac.cn), Kong, L. (konglp@hpstar.ac.cn), Yang, W. (yangwg@hpstar.ac.cn).

the well-known Shockley–Queisser theory [24], it is highly desirable to tune these 2D hybrid perovskites, and some other 0D perovskites quantum dots [25,26] and double perovskites [27,28], to narrow their bandgap for broader solar spectrum absorption and then reduce the gap between high performance and good stability.

Composition engineering is a conventional route to improve the material properties of metal halide perovskites for better photovoltaics applications. However, compositional modification suffers from challenges, such as the significantly shortened carrier lifetime (~50 ps), and thus, considerable loss of photovoltage upon the replacement of Pb by Sn, or the largely widened band gap, and hence, weaker light absorbance when I is substituted with Br or Cl, or interior stability due to the substantial substitution of I with Br [29–31]. Therefore, urgently exploring an alternative way to fundamentally understand and improve the material properties is crucial to their potential long-term commercial use; i.e., gaining better photovoltaic merits of 2D hybrid perovskites, OD perovskite quantum dots, and double perovskites while retaining, if not improving, their desirable environmental stability, particularly their moisture tolerance.

As a powerful and clean tool for continuously tuning the crystal lattice and electronic wave functions [32–34], hydrostatic pressure is promising to precisely modulate the crystal lattice of HPs and pinpoint their electronic behaviors with atomic-level understanding [33–90]. Pressure is an effective post-synthesis method to tune key material properties by modulating their lattice structure in a precise and controllable manner. Pressure can realize simultaneous bandgap narrowing and carrier-lifetime prolongation [46], PL intensity enhancement [86], and the ambientmemorized retainability from high-pressure conditions [57], thus



FIGURE 1

Pressure engineering on photovoltaic perovskites focuses on the core region among "Three Greens" (Green materials, Green energy, and Green engineering).

achieving better materials by design toward tunable, improved, and retainable performance for next-generation photovoltaic and semiconductor systems. Moreover, pressure is a critical thermodynamic parameter that can provide an ideal platform to investigate the structure-properties relationship comprehensively, which provides a direct guideline for next-generation high-performance photovoltaic materials. In situ characterizations of structure and properties under compression and decompression conditions in HPs can also be a novel method for exploring now electronic phenomena, such as the direct-indirect bandgap transition [69], metallization, and even superconductivity, [54] which have so far been restricted to their oxide analogs. Therefore, there is a critical need to review and understand the fundamental material properties of the perovskite absorbers, including traditional bulk 3D perovskites and novel 2D/0D/double perovskites under pressure conditions, and explore the possibility of pressure/strain engineering to modify energy materials for photovoltaic applications. Fig. 1 shows the field of this study, explaining that research is located in the core region of "Three Greens" (Green materials-perovskites; Green energy-solar energy; and Green engineering-high pressure).

Pressure-induced structural evolution

Crystalline phase transitions

In thermodynamics, the state of matter is determined by the given set of physical conditions, including pressure (*P*), volume (*V*), and temperature (*T*), which can be described by an equation of state (EOS) relating state variables [91]. By fitting cell volume data obtained from high-pressure diffraction measurement to the equation of state, the bulk modulus (K_0) can be derived. For HPs, the K_0 values of ambient phases have been estimated to be less than 30 GPa [92,93], one order of magnitude smaller than their oxide perovskite counterparts [94,95]. Lee et al. reported that FASnI₃ has the smallest bulk modulus ($K_0 = 8.0$ (7) GPa) observed in any reported perovskite-related structure [38]. These observations confirmed that the "soft" nature of halide perovskites with high compressibility makes the structural and functional modifications under low levels of applied pressure promising.

In the 1990s, the pressure-temperature phase relations of MAPbX₃ (X = Cl, Br, I) were studied using differential thermal analysis (DTA) apparatus and dielectric measurements. The P-T phase diagrams (100 K < T < 360 K; 1 atm < P < 700 MPa) were suggested although detailed structure information cannot be accurately determined due to the lack of diffraction data [35,36]. In the 2000s, to further investigate organic-inorganic hybrid HPs under high pressure, a suite of powerful characterizations, such as in situ neutron and synchrotron x-ray diffractions, were employed, and pressure-driven structural changes at atomic level were revealed. Since 2009, the metal trihalide perovskites have emerged as excellent absorbers for photovoltaic applications, triggering an unprecedentedly rapid growth in highpressure structural investigations of these materials in the last three years. Wang et al. reported the phase stability of MAPbBr₃ powders up to 34 GPa and suggested two phase transitions below 2 GPa (from Pm3m (1 atm) to Im3 at ca. 0.25 GPa, and then to *Pnma* at 1.8 GPa), where the $Pm3m \rightarrow Im3$ is believed to be a

first-order phase transition with an abrupt volume collapse of 6% [41], although it is not consistent with results reported in refs. [40] and [67]. In previous neutron experiments, Swainson et al. demonstrated that MAPbBr₃ undergoes a $Pm\bar{3}m \rightarrow Im\bar{3}$ phase transition, but at ca. 0.9 GPa and without an obvious cell volume discontinuity [40], which is further supported by Szafrański and Katrusiak's study using a laboratory diffractometer operated with graphite-monochromated Mo K α radiation [67].

In other MA-based lead halides, such as MAPbI₃ and MAPbCl₃, there are also some discrepancies regarding highpressure structural properties. For example, the isostructural phase transition of MAPbCl₃ between two cubic phases is observed in Ref. [51], but argued by Ref. [67], which suggested a symmetry lowering. The synchrotron single-crystal XRD experiments and structural refinements of MAPbI₃ demonstrated a tetragonal *I4/mcm* to orthorhombic *Imm2* phase transition lower than 0.4 GPa [46], which can be evidenced by the prominent peak splitting between the (330) and (3–30) Bragg reflections in the high-pressure phase (Fig. 2a). Alternatively, also using synchrotron single-crystal XRD, Jaffe et al. reported the highpressure phase is cubic symmetry $Im\bar{3}$, and the ambient phase is orthorhombic *Fmmm*, although their density functional theory (DFT) calculations on the electronic band structure based on the proposed crystalline structure cannot be correlated with the optical results presented in the same article [44].

Table 1 lists the pressure-induced crystalline phase transitions in various photovoltaic HP-related materials. Some common characteristics can be derived from these high-pressure works by different research groups: 1) The pressure-driven phase transitions can be described as the distortion, titling, or rotation of the $[BX_6]^-$ octahedra. 2) The first pressure-induced phase transition of HPs, especially for organic–inorganic hybrid HPs, usually occurs in the low-pressure range, being an order of less than a few GPa, which is associated with their low bulk modulus and high-level mechanical response to pressure or strain. 3) Compression will induce amorphization when the applied pressure is



FIGURE 2

Pressure-driven phase transitions in various HPs. (a) Single-crystal diffraction characterization of MAPbl₃. From left to right: SCXRD pattern at 0.4 GPa at the center detector position; zoomed-in views of SCXRD patterns at 0.4 GPa and 1 atm, respectively, from which splitting between the (330) and (3–30) reflections and suggested symmetry lowering were demonstrated at high pressure; Comparison of Pb-I frameworks between 1 atm and 0.4 GPa. (b) Pressure dependence of lattice volume of $Cs_2AgBiBr_6$. (c) and (d): Transmission electron microscope (TEM) images and pressure-driven structural evolution in MAPbBr₃ nanocrystals, respectively. Revised from [46,58], and [82] with permission.

Materials	Pressure-induced crystalline phase transitions	Characterization method	PTM [*]	Refs
MASnl₃	$Pm\overline{3}m$ (1 atm) $\rightarrow Im\overline{3}$ (0.81 GPa) $\rightarrow Immm$ (3.11 GPa)	Synchrotron PXRD**	Fluorinated polymer	[38]
MAPbBr ₃ ***	$Pm\overline{3}m$ (1 atm) $\rightarrow Im\overline{3}$ (below 1 GPa)	Neutron diffraction	2-Propanol-D ₈	[40]
MAPbBr ₃	Pm_3m (1 atm) $\rightarrow Im_3$ (0.25 GPa) $\rightarrow Pnma$ (1.8 GPa)	Synchrotron PXRD	No PTM	[41]
MAPbl ₃ MAPbl ₃ MAPbBr ₃	<i>I4/mcm</i> (1 atm) → <i>Imm2</i> (0.26 GPa) <i>I4/mcm</i> (1 atm) → <i>Imm2</i> (0.4 GPa) $Pm\overline{3}m$ (1 atm) → $Im\overline{3}$ (0.5 GPa)	Synchrotron PXRD Synchrotron SCXRD** Synchrotron SCXRD**	Helium Mineral oil Mineral oil	[42] [46] [46]
MAPbl ₃	$14/mcm$ (1 atm) $\rightarrow Im\overline{3}$ (0.4 GPa) $\rightarrow Immm$ (2.7 GPa)	Synchrotron PXRD	-	[45]
MAPbl₃	$14/mcm$ (1 atm) $\rightarrow 1m3$ (0.45 GPa) $\rightarrow 1m3$ (2.71 GPa)	SCXRD	Propanol	[48]
MAPbBr ₃	$Pm\bar{3}m$ (1 atm) $\rightarrow Im\bar{3}$ (1.7 GPa)	Synchrotron SCXRD	Helium	[44]
MAPbl₃	Fmmm (1 atm) $\rightarrow Im\overline{3}$ (0.7 GPa)	Synchrotron SCXRD	Helium	[44]
MAPbBr ₃	$Pm\bar{3}m$ (1 atm) $\rightarrow Im\bar{3}$ (0.9 GPa)	Synchrotron PXRD	Helium	[44]
MAPbl₃	Fmmm (1 atm) $\rightarrow Im_3^2$ (0.3 GPa)	Synchrotron PXRD	Helium	[44]
MAPbI _{1.2} Br _{1.8}	$Pm3m$ (1 atm) $\rightarrow Im3$ (2.7 GPa)	Synchrotron PXRD	Helium	[44]
MASnl₃	$P4mm$ (1 atm) $\rightarrow Pnma$ (0.7 GPa)	Synchrotron PXRD	Silicone oil	[47]
FAPbBr ₃	$Pm\bar{3}m$ (1 atm) $\rightarrow Im\bar{3}$ (0.53 GPa) $\rightarrow Pnma$ (2.2 GPa)	Synchrotron PXRD	Silicone oil	[50]
MAPbCl ₃	$Pm\overline{3}m$ (1 atm) $\rightarrow Pm\overline{3}m$ (0.8 GPa) $\rightarrow Pnma$ (2.0 GPa)	Synchrotron PXRD	Silicone oil	[51]
	$P2_1/a \text{ (1 atm)} \rightarrow P2 \text{ (6.5 GPa)}$	Synchrotron PXRD	Silicone oil	[59]
Cs ₂ AgBiBr ₆	$Fm3m$ (1 atm) $\rightarrow I4/m$ (3.1 GPa)	Synchrotron PXRD		[58]
FAPbl ₃	$Pm\overline{3}m$ (1 atm) $\rightarrow P4/mbm$ (0.49 GPa)	Synchrotron SCXRD	Silicone oil	[66]
MAPbBr ₃	$Pm3m$ (1 atm) $\rightarrow Im3$ (0.75 GPa)	SCXRD	Propanol	[67]
MASnCl ₃	$P1 (1 \text{ atm}) \rightarrow P1 (1.0 \text{ GPa})$	Synchrotron PXRD	Silicone oil	[68]
CsPbBr.****	$Pm3m$ (1 atm) $\rightarrow Imm2$ (0.34 GPa) $\rightarrow Immm$ (1.67 GPa)	Synchrotron PXRD	Silicone oil	[70]
CsPbBr	$Pm3m$ (1 atm) $\rightarrow Pbnm$ (1.54 GPa)	Synchrotron PXRD	Silicone oil	[75]
MAPhBr.	$Pm3m$ (1 atm) $\rightarrow Pbnm$ (1.2 GPa)	Synchrotron PXRD	Helium	[75]
	$Pm3m$ (1 atm) $\rightarrow Im3$ (0.85 GPa)	Synchrotron PXPD	Argon	[70]
	$Pm3m$ (1 atm) $\rightarrow Im3 + Pnma$ (0.85 GPa)	Synchrotron PXPD	No PTM	[70]
	$Pm3m$ (1 atm) $\rightarrow Im3$ (0.4 GPa) $\rightarrow Pnma$ (1.5 GPa)	Synchrotron PXPD	Silicono oil	[70]
	$Pm3m$ (1 atm) $\rightarrow Pbnm$ (0.39 GPa)	Synchrotron PXPD		[/0]
	$Pm3m$ (1 atm) $\rightarrow Im3$ (0.99 GPa) $\rightarrow Pnma$ (2.41 GPa)	Synchrotron WAXS**	- Toluono	[02]
	$Pm3m$ (1 atm) $\rightarrow Im3$ (0.6 GPa)	Synchrotron DVDD		[09]
	$Pm3m$ (1 atm) $\rightarrow P2_1/m$ (3.9 GPa)			[ð4]
Cs ₂ SnBr ₆	no phase transition observed till 19.6 GPa	Synchrotron PXRD	Silicone oil	[85]

* PTM denotes pressure transmitting medium.

** PXRD denotes powder X-ray diffraction; SCXRD denotes single crystal X-ray diffraction; WAXS denotes wide angle X-ray scattering.

*** The sample is fully deuterated.

**** The samples are nano crystals.

high enough, and perovskites will revert to crystalline forms after the pressure is totally released (this will be discussed later in the text).

For the discrepancies of the high-pressure structural properties in a given material, possible origins can be proposed. It should be noted that the structures of HPs have dynamic characteristics. It has been experimentally shown that during decompression, the crystalline retention of MAPbI₃ is dependent on the peak pressure under compression (Fig. 3a) [45]. Furthermore, Szafrański and Katrusiak confirmed that the structure of MAPbX₃ is both pressure- and time-dependent (Fig. 3b) [67]. Such results tell us the structural information obtained from diffraction experiments is determined not only by the technique employed but also when the sample is detected. The slow kinetics of HPs requires us to wait to conduct experiments until after materials are thermodynamically stable at pressures, reminds us of the strong possibility of low-pressure and high-pressure phases coexisting, and also provides opportunities to study their timedependent properties. The significant effects of non-hydrostatic stress on the structural properties of HPs mean the pressuretransmitting medium (PTM) used in high-pressure experiments will affect the observations (Fig. 3c) [76]. For MAPbBr₃, using PTM Ar and Ne postpones the occurrence of amorphization compared to non-hydrostatic compression without any PTM. Plus, attention should be paid to the twinning characteristic in crystals [67,99], the strength of the background signal in high-pressure powder XRD experiments, as well as the possible radiation damage in synchrotron diffractions [100], all of which could



Some factors that affect high-pressure structures in HPs. (a) Schematic illustration of high-pressure crystal phases of MAPbl₃; during decompression the crystallographic restoration behavior is strongly dependent on the peak-pressure achieved upon compression. (b) Transmitting-illumination photographs of MAPbBr₃ and MAPbCl₃; the time-dependent characteristic can be observed, suggesting the structural transformations are dynamic processes. c) Non-hydrostatic pressure effects on the structure of MAPbBr₃ at 1.6 GPa; at non-hydrostatic (no PTM) and quasi-hydrostatic (PTM: He) pressure conditions different space groups are concluded based on respective PXRD data. Revised from [45,67], and [76] with permission.

negatively affect the accurate determination of high-pressure phase and symmetry.

FIGURE 3

Besides HPs with ABX₃ a three-dimensional framework, pressure also profoundly alters the structure of other HPs, such as double perovskites (Fig. 2b), zero-dimensional (0D) perovskites quantum dots or nanocrystals (Fig. 2c and d), and layered twodimensional (2D) perovskites. It is well known that the doubleand low-dimensional perovskites exhibit enhanced phase stability, improved moisture tolerance, and mixability with other functional materials [96-98], and in particular, their pressuredriven structural response is significantly different from their 3D counterparts. For the double perovskite Cs₂AgBiBr₆, the phase transition from Fm3m to I4/m is associated with an obvious cell volume collapse as convinced by XRD data refinements, and during the phase transition, the splitting of the Ag-Br and Bi-Br bond shifts indicates (Ag, Bi)Br₆ octahedral distortion [58]. In addition, both FA-based and MA-based perovskite nanocrystals show distinct pressure-induced phase transition behavior compared to their respective 3D bulk materials [82,89], and for 2D perovskites, two distinct regimes of compression dominated by the softer organic and less compressible inorganic sub-lattices

have been identified, where the former and latter are controlled by layer-to-layer compression and inter-layer compression, respectively [56].

Disorder and amorphization

A lack of long-range order characterizes amorphous materials. There are several standard methods to generate amorphous states, including fast cooling of the liquid to kinetically hinder the crystallization [101–102], creating enough defects in the crystalline materials [103], and using hydrostatic pressure or shock wave to induce amorphization when the melting curve shows a downward trend with pressure [104]. It is well recognized that pressure-induced atomic disorder and amorphization are common in various HP materials. Due to higher interatomic repulsive forces under compression, the diffusion of atoms is reduced, and the phase transitions by lattice reconstruction are not favored at high pressure. Thus, presumably the pressure-induced amorphization in HPs belongs to displacive phase transitions via an atomic distortion stage rather than reconstructive ones, and breakage of the primary interatomic bonds are not required to interconvert the crystal structures.

Furthermore, the amorphization in HPs depends on pressure, temperature, the amount of non-hydrostatic stress, as well as the thermodynamic pathways, where some metastable and intermediate phases may be involved. Also, one can see that the observation of amorphization could be technique specific since various methods give information, which reflects their typical length scales. At high pressures, we usually observe "X-ray amorphous" (length scale is over $1 \mu m$) in HPs and can still detect clear spectroscopic features of the crystalline state by Raman and/or IR characterizations reflecting the information from 0.01 to 0.1 μm .

It is worth noting that novel phenomena, improved properties, and structure-property relationships can be derived from amorphization observations. Lü et al. reported the enhanced structural stability of MASnI₃ via pressure-induced amorphization and recrystallization (Fig. 4a–c) [47]. After the first compression–decompression cycle, the sample at ambient pressure from a high-pressure amorphous state exhibited more uniform and fine crystal grain characteristics. During the second compression up to 31 GPa, no amorphization was observed while the perovskite phase was maintained, from which enhanced structural

stability is demonstrated and associated with the three-fold increase in electrical conductivity and photocurrent enhancement. For 2D perovskites, in situ high-pressure diffraction measurements on the Ruddlesden-Popper hybrid perovskites $[(BA)_2(MA)_{n-1}Pb_nI_{3n+1},$ $(C_4H_9NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$ n = 1, 2, 3, 4] establish a comprehensive picture of *n*-dependent pressure-driven distortion behavior and further structure-property relationships (Fig. 4d) [90]. Such pressure-driven distortions are not only suggested by the broadened XRD reflections but also further supported by the broadened mid-IR peaks (Fig. 4e) [56]. Interestingly, for 2D perovskites (BA)₂(MA)₂Pb₃I₁₀, the highest level of disorder during pressure cycle was observed upon decompression at 6 GPa rather than during the compression stage even though the pressure is much higher (27 GPa) (Fig. 4f) [90]. This discovery explains the obvious blue-shift in the optical bandgap during decompression. A large number of materials turn amorphous under compression. Such decompression-induced amorphization in 2D perovskites confirms that the residual crystalline characteristics could disappear on the release of pressure in some organic crystals, which has been reported in inorganic perovskite [105], alloys [106,107], and carbon materials



FIGURE 4

Pressure-driven amorphization and order–disorder transitions in HPs. (a)–(c): Pressure-driven structural evolutions of MASnl₃ upon compression and recompression. A structurally stable characteristic is suggested in the decompressed specimen, resulting in the delayed amorphization under re-compression. (d) Summary of order–disorder pressure points of various 2D HPs, including (BA)₂Pbl₄ (n = 1), (BA)₂MAPb₂l₇ (n = 2), (BA)₂(MA)₂Pb₃l₁₀ (n = 3), and (BA)₂(-MA)₃Pb₄l₁₃ (n = 4). (e) The order–disorder transitions can be evidenced by the broadened XRD and mid-IR peaks (see inset) at higher pressures. (f) PXRD pattern images of (BA)₂(MA)₂Pb₃l₁₀ (n = 3) measured during compression and decompression; the highest level of amorphous state occurs during decompression at 6 GPa, suggesting a structural reconstruction process. Revised from [47,56], and [90] with permission.

[108]. Amorphization upon decompression is associated with the metastable nature of the high-pressure phase at low pressures, and if the lifetime of the metastable state is sufficiently long enough [101]. Therefore, in 2D perovskites [90], the highpressure structure (27 GPa) likely becomes sufficiently metastable upon compression to collapse to an amorphous phase around 6 GPa. This interpretation agrees with the metastable nature of the same 2D materials at ambient conditions after applied pressure is completely removed [90]. We also note that the magnitude of pressure distortion is related to the structure of specific materials. The results of single-crystal x-ray diffraction experiment confirm that all Bragg spots disappear at 4.6 GPa for MAPbI₃ [46], while significant crystalline characteristics can be detected in FAPbI₃ up to 7.0 GPa [57]. CH₃NH₃PbI₃ is only aligned linearly along one dimension. Thus, hydrostatic pressure will lead to inhomogeneous contraction of Pb-I-Pb in three dimensions, then the phase transition and further atomic distortion and amorphization are triggered in the low-pressure regions. Alternatively, FAPbI₃ is composed of large $HC(NH_2)^+_2$ with cationic charge distributed over its structure via the π system and exhibits linear Pb-I-Pb bonds along all three dimensions. Thus, the response of the P-I-Pb bonds to pressure is spatially quasihomogeneous, and the postponement of pressure-induced distortion/amorphization can be expected.

Local structure

Spectroscopy is a powerful technique to detect local distortion in HPs. Raman spectra must obey definitive selection rules based on group theory, thus, if the forbidden modes are observed, local distortion from the average symmetry can be demonstrated [109,110]. The frequency region where phonon modes appear depends on the structural symmetry and the intramolecular modes from methylamine. Raman modes appear in a higher frequency region and can also serve as an indication of structural change. At ambient conditions, MAPbBr₃ exhibits a cubic phase where none of the phonon modes are Raman active, while at high pressures above 0.8 GPa, phonon modes were observed, indicating a local symmetry change and structural transition [39].

Spectroscopy also provides an opportunity to explore the structural evolution of organic parts in hybrid perovskites because X-rays are scattered much less efficiently by light atoms in an organic group than heavy inorganic atoms. Moreover, neutron scattering experiments are time-consuming and require fully deuterated samples. Under compression, we witnessed various mid-infrared (IR) vibrational modes (Fig. 5) from organic moiety shift and broaden, which can be explained by the intensified interatomic force, and the decrease in the crystalline long-range order [46]. For MAPbI₃, no significant changes in fre-



FIGURE 5

Various vibration modes in MAPbX₃, including CH₃ stretch, C–N stretch, NH₃ bend, and NH₃ stretch. Yellow, blue, and gray balls represent the carbon, nitrogen, and hydrogen atoms, respectively.

quency were observed in the low-pressure phase. A notable blueshift in the C–H stretching mode was observed in the highpressure phase where there was strenuous repulsion between the inorganic PbI_3^- framework and the electron waves on the H atoms in the methyl group. The opposite red-shift trends for the N–H stretching and bending modes can be attributed to pressure-induced lattice shrinkage, enhancing the electrostatic attraction between the cationic charge on the nearly naked protons in NH₃⁺ and their neighboring anionic charge on the $PbI_3^$ framework, then slowing down the modes related to NH₃⁺.

Pressure-tailored physical properties and structureproperty relationship

Bandgap

High-efficiency solar cells require a small V_{OC} deficit, which is defined by $(E_g/q) - V_{OC}$ [15]. Here, E_g is the optical bandgap, qis the elemental charge, and V_{OC} is the open-circuit voltage. According to the Shockley–Queisser theory, the optimum bandgap energy should be between 1.3 and 1.4 eV [24]. Thus, narrowing down the bandgap of HPs from current magnitudes (more than 1.5 eV) is critical to achieve the efficiency limit of ~33.7%. Alternatively, enlarging the bandgaps in HPs could have applications in high-power techniques, light-emitting

diodes, and lasers. As discussed in Section II, pressure significantly changes the lattices of HPs, thus, inevitably tuning the boundary conditions of electronic wave functions and affecting the bandgap. There are two methods to measure the bandgap at high pressures: (1) positioning the peak energy position of in situ high-pressure photoluminescence (PL); and (2) calculating the bandgap via in situ high-pressure optical absorbance spectroscopy using Tauc Plot linear fittings. In PL, the bandgap must be carefully calculated by taking into account the binding energy of the exciton, overlap of the emission and absorption modes, and the Stokes shift. Furthermore, it has been observed that PL intensities weaken until they are finally undetectable in HPs under compression [60], which can make bandgap determinations at high pressures unreliable. However, high-pressure PL measurements provide information on emission enhancement and quantum yield-related properties, which have been reported in compressed 2D and 0D HPs [56,86].

Fig. 6a summarizes the bandgap in various HPs under compression, demonstrating that: (1) pressure is a powerful thermodynamic route that can significantly alter the bandgap in all HPs, even in mild pressure ranges less than 1 GPa; (2) essential variations of the bandgap with pressure, including both blueshift and red-shift, can be realized in a material, and (3) unlike the structural properties, there is not an apparent discrepancy



FIGURE 6

Pressure dependence of bandgap in HPs. (a) Summary of bandgap evolutions in various HPs. (b) Bandgaps in various APbl₃ perovskites; the average Pb—I—Pb bond angle plays a crucial role in bandgap magnitude. (c) Schematic illustration of Pb—I—Pb bonds under compression; both bond angle decrease and bond length shortening could occur, leading to bandgap red-shift and blue-shift, respectively. Revised from [90] and [113] with permission. Data in (a) are from [37,45,46,51,54,56–58 67,70,71,75,78,89], and [90].

in the bandgap among various research groups. To fully understand the strong pressure dependence of the bandgap, the dominating factors of the bandgap in HPs and the pressure-driven structural evolutions should be comprehensively considered. For a HP with $[BX_6]^-$ octahedra, the primary mechanism controlling the bandgap is the overlap of electronic wave functions between the metal B and the halide X ions, while the A cations do not directly contribute to the electronic properties [111,112]. However, we cannot conclude that A cations do not affect bandgap since they have a strong influence on the stability and tilting of the $[BX_6]^-$ octahedra and then affect the bandgap indirectly via steric and Coulombic interactions. Stoumpos and Kanatzidis analyzed the bandgap of various ABX₃ perovskites, where "BX3" is identical to be "PbI3" and A cation changes (Fig. 6b) [113]. They observed a clear decreasing trend in the bandgap while deviation from the ideal structure increased, which can be assessed by the Pb-I-Pb bond angle of less than 180°, and a smaller overlap of the Pb and I orbitals. The bandgap is determined by the positions of the conduction band minimum (CBM) and valence band maximum (VBM). The electronegativity between Pb and I is relatively small (Pb: 2.33 vs. I: 2.66), leading to the strong Pb s and I p antibonding character in the VBM, whereas the CBM has a mostly nonbonding Pb p character. Therefore, the Pb s and I p orbital overlap will push up the VBM while not affecting the CBM, then narrow down the bandgap. Upon compression, the Pb-I-Pb bond length shortens and the Pb–I–Pb bond angle of [BX₆]⁻ octahedra decreases, leading to orbital overlap enhancement and retrogression, respectively, and thereby accounting for the optical bandgap red-shift and blue-shift (Fig. 6c).

The proposed mechanisms of the pressure-driven bandgap evolution above are consistent with the experimental observations, as shown in Fig. 6a. Taking FAPbI₃ as an example [57], in the low-pressure phase the three Pb-I-Pb bond angles in the unit cell remain at nearly 180°, but the bond length shortens under pressure. Then, the Pb s and I p orbital coupling enhances, leading to continuous bandgap narrowing down to 1.337 at 2.1 GPa, reaching the optimum bandgap magnitude required by the Shockley-Queisser model. The following blue-shift of the bandgap in compressed FAPbI₃ can be attributed to the lattice distortion and atomic displacement, which lead to a misaligned Pb-I-Pb bond and less coupling between the Pb s and I p orbitals. Such an atomic distortion-driven bandgap blue-shift phenomenon has been further evidenced in compressed 2D HPs. For (BA)₂(MA)Pb₂I₇, there is a blue-shift pressure range (4-13 GPa) between two regions of bandgap narrowing, which can be interpreted as atomic distortion that lowers the lattice symmetry and causes less Pb s and I p orbital coupling [56].

Carrier lifetime

According to the Shockley–Queisser theory, the open-circuit voltage V_{OC} can be described as [114]:

$$V_{\rm OC} = \frac{kT}{q} \ln\left(\frac{J_{\rm SC}}{J_0}\right) = \frac{kT}{q} \ln\left(\frac{J_{\rm SC}N_{\rm D}\tau_{\rm eff}}{qn^2d}\right) \tag{1}$$

Here, *k* is the Boltzmann constant; *T* is the temperature; J_{SC} is the short-circuit current density; J_0 is the initial current density; N_D is the doping concentration, τ_{eff} is the effective carrier recom-

bination lifetime; *n* is the intrinsic carrier concentration; *d* is the thickness of the light absorber, and *q* is the charge of an electron. From Eq. (1) it is clear that prolongation of the carrier recombination lifetime will lead to greater $V_{\rm OC}$, and thus, a small $V_{\rm OC}$ deficit and higher PCE can be expected.

Interestingly, carrier recombination lifetime prolongation in various HPs including MAPbBr₃, MAPbI₃, FAPbI₃, and CsPbBr₃ nanocrystals has been realized through compression (Fig. 7a-e) [46,57,71]. Under mild pressures below 0.3 GPa, a 70–100% increase in τ_{eff} has been discovered in MAPbI₃ single crystal and powders by in situ high-pressure time-resolved PL measurements (Fig. 7a-c) [46], which can be well correlated with the structural change of materials. Based on the in-gap electronic state spectrum measurement by Adinolfi et al. [115], the density of the trap state was confirmed to be localized in energy closed to CBM and VBM. The shallow states become even shallower as pressure increases due to the ascendance of the VBM (Fig. 7d). Then, a larger portion of recombination becomes radiative, and a longer carrier lifetime is consequently expected. Recently, an unprecedentedly long carrier lifetime up to 484-2272 ns was reported in FAPbX₃ (X = Br and I) [13,116], suggesting the same low-density and shallow trap states as MAPbI₃. Thus, it is not strange to observe the carrier recombination lifetime prolongation in compressed FAPbI₃ [57] (Fig. 7e). Wu et al. observed that the density of excitonic traps increases with quantum confinement by investigating various 2D HPs [133]. A critical origin of trap states is electron-phonon coupling at the surfaces/interfaces. In 2D HPs, there are a large number of organic/inorganic interfaces, which play similar roles to the exposed surface of 3D HPs in carrier recombination. The high density of the trap state is not easily tuned by pressure, giving rise to the absence of carrier lifetime prolongation in 2D HPs [56].

In addition, the effect of pressure-induced defects on lifetime should not be ignored. Wang et al. observed five times faster charge carrier recombination in a MAPbI₃ film (Fig. 7f) and correlated it with the indirect-direct bandgap transition [69]. The pressure-driven carrier lifetime shortening in the MAPbI₃ thin film cannot be attributed to the intrinsic lattice deformation effect when considering the pressure-driven carrier lifetime prolongation in MAPbI₃ single crystals [46]. Compared to single crystal, thin films exhibit different mechanical behavior, including intrinsic stress, elastic bulk modulus, and yield strength, which can be understood by the partially confined material nature. The mechanical property will be significantly affected by the applied pressure, and defects will be easily generated in thin films, especially in the thin film/substrate interface region due to the atomic distortion associated with lattice mismatch. Such pressure-generated defective states tune into the charge-carrier recombination centers and then dramatically decrease the carrier lifetime in thin films.

Besides the carrier recombination lifetime, a simultaneous prolongation of carrier relaxation lifetime and Auger recombination lifetime in HPs has been suggested by Liu et al. through *in situ* high-pressure femtosecond transient absorption spectroscopy experiments (Fig. 7g–j) [80], further supporting that pressure is an effective route to modulate the carrier dynamics in HPs. The inflections of pressure-dependent lifetimes occur at the pressure-induced phase transitions, demonstrating that the



FIGURE 7

Pressure dependence of carrier lifetime in HPs. (a)–(c): *In situ* high-pressure TRPL measurements on a MAPbl₃ single crystal at 1 atm (a), 0.3 GPa (b), and 1.0 GPa (c), in which the prolongation of carrier recombination lifetime is demonstrated. (d) Schematic illustration of the correlation between the band edges approaching and carrier-lifetime prolongation in MAPbl₃. (e) Summary of carrier recombination lifetime prolongation in various HPs crystals and powders. (f) Carrier recombination lifetime measurements of MAPbl₃ thin films. (g) Schematic illustration of the *in situ* high-pressure femtosecond transient absorption spectroscopy measurement. (h) Representative dynamic trace extracted from the transient absorption spectra at high pressure. (i) Pressure dependence of transient absorption kinetic lifetimes for carrier relaxation. (j) Pressure dependence of transient absorption kinetic lifetimes for phonon scattering and Auger recombination. Revised from [46,69], and [80] with permission.

crystal structure controls the electronic band structure. Although Auger recombination may not be the core factor to affect chargecarrier concentrations in solar cells, it has significant influence in laser or solar-concentrator applications [117–119].

Photocurrent and electrical resistance

Excellent progress has been made in pressure-tailoring electronic properties of HPs. It is not surprising that change of electrical resistance reaches 2–5 orders of magnitude upon compression in HPs, because pressure is a powerful tool to drive many electronic transformations in condensed matters, such as the metallization in 2D transition metal dichalcogenides, even though no structural phase transition occurs [120]. Furthermore, by *in situ* high-pressure alternating-current impedance spectroscopy, Yan et al. proposed the mechanisms of pressure-tuned electrical

transport properties in MAPbBr₃ (Fig. 8a–c) [72]. By analyzing the related equivalent circuit and fitting the measured impedance spectra, electrical parameters regarding ions and electrons migrations were derived. Mix conduction behavior was evidenced, in which initially ionic conduction is the predominant process, whereas electronic conduction becomes the dominant factor above 3.3 GPa. Of particular interest is that at mild pressures below than 0.4 GPa, namely in the ambient phase, compression gives rise to ion migration enhancement, which is evidenced by the increased frequency of the inflection point from local vibration to long-distance diffusion under the electric field. At least two reasons can be proposed to understand this phenomenon: (1) pressure changes the vacancy distribution in perovskite and then controls the process of ion migration, and (2) pressure provides defects that are critical for enhancing the



FIGURE 8

Pressure-driven evolutions of electrical and photo responsiveness in HPs. (a) The measured and simulated impedance spectrum of MAPbBr₃ at 1.0 GPa. (b) The pressure dependence of electrical resistance of MAPbBr₃. (c) The inflection frequency as a function of applied pressure. (d) and (e) The measured electrical resistance and photocurrent of MAPbBr₃ as a function of pressure up to 30 GPa. (f) and (g) Photocurrents of MASnl₃ upon first compression and second compression at low pressure (0.7 GPa) and high pressure (\sim 25 GPa). Revised from [41,47], and [72] with permission.

ionic conductivity. The pressure-driven changes in electrical resistance of HPs are usually discontinuous, which can be attributed to structural phase transitions.

A rising hypothesis in high-pressure HP research questions whether the HPs still exhibit an electrical response to visible light under compression or not, which is crucial for their lightharvesting ability for real photovoltaic applications. Although there is no report to date on any HP-based photovoltaic device at pressure conditions, our answer is very promising based on the results about detectable photocurrent in HPs under compression, even in their high-pressure amorphous states. Wang et al. first investigated the photocurrent response to pressure of HPs and demonstrated that in MAPbBr₃ the photocurrent has a visible light on–off switch characteristic that can persist to the highest pressure reached in their experiment (30 GPa), although it is suppressed due to the structural disorder nature (Fig. 8d–e) [41]. The occurrence of photocurrent at high pressures has been further confirmed in other HPs. Interestingly, upon recompression, the pressure-treated $MASnI_3$ exhibits a significantly higher photocurrent than the original sample in both low- and high-pressure regions, associated with the improved structural stability (Fig. 8f–g) [47].

Pressure-driven novel properties in HPs

In this section, we will discuss the novel properties in pressuretreated HPs, including both the ambient improvement/modification in pressurized samples, as well as the unprecedented behavior in known materials at high pressures. The former is crucially important for practical applications, and the latter sheds some light on future material design for multi-functional HPs.

Ambient properties after pressure treatments

It is rare that the structure and properties of chemical compounds under high pressure can be retainable after decompression, and the pressure-driven phase transformation and amorphization were previously believed to be reversible upon decompression. However, a recent report on the structural analysis of MAPbI₃ at ambient pressure after releasing pressure suggests a retainable structure with the high-pressure Imm2 space group [42]. Subsequently, the increased degree of MAPbI₃ cubicity compared to original orthorhombic MASnI3 perovskites was observed, which also suggests a tunable structure after pressure treatment [47]. Since pressure-induced disorder, atomic distortion, and amorphization are unavoidable single-crystal diffraction measurements cannot identify the crystalline structure in samples after pressure is removed. However, we can conclude that structural modifications by pressure treatments are possible, at least on the magnitude of lattice parameters and increased homogenization of grains, which have been evidenced by detailed Rietveld refinements on powder diffraction data and smoother diffraction rings in XRD pattern [47,57], respectively. These discoveries impel scientists to continuously study the ambient improvement of HPs using pressure-related strategy.

The study on FAPbI₃ perhaps provides the first example of pressure-driven bandgap modification after pressure treatment (Fig. 9a, from 1.489 eV in an as-prepared sample to 1.447 eV after compression-decompression cycle) [57], which can be attributed to the interplay between the Pb-I-Pb bond angle and bond length with the valence band energy. Such a discovery of retainable bandgap narrowing upon the release of pressure has been further confirmed in other HPs, including Cs₂AgBiBr₆ and 2D perovskites [56,58,90], paving a practical and clean pathway toward better materials by design for more efficient photovoltaic materials. Comprehensive investigations together with DFT calculations on high-pressure bandgap engineering of 2D perovskites reveal that the origin of bandgap narrowing comes from metastable states through structural amorphization under compression followed by recrystallization via decompression. These factors create enduring bandgap narrowing by as much as 8.25% can be reached (Fig. 9b) [90].

Pressure treatments also effectively tune the electrical conductivity of the recovered HPs. In decompressed MASnI₃, the electrical conductivity is three times higher than that of a pristine sample. This conductivity is associated with the higher carrier mobility rooted in higher crystallographic symmetry in pressure-treated samples, as well as the smaller cell volume and smaller carrier effective mass (Fig. 9c–e) [47].

The pressure effects on the structural, mechanical, and functional properties in nanomaterials are proven to be significantly different from their bulk 3D counterparts. Nagaoka et al. reported the pressure processing and phase transitions of CsPbBr₃ nanocube superlattices (NC-SLs) (Fig. 9f–j) [61]. Of particular interest is that the individual CsPbBr₃ NC-SLs transfers into 2D nanoplatelets (NPLs) with a uniform thickness. Xiao et al. further convinced such a geometrical morphology effect by comparing the high-pressure behavior of bulk 3D CsPbBr₃, CsPbBr₃ nanowires, and CsPbBr₃ nanocrystals [71]. The synthesized CsPbBr₃ NPLs exhibit 1.6-fold more PL enhancement than starting NC-SLs and are thus promising for various potential applications [61]. Besides all inorganic CsPbBr₃, pressure-derived morphological and functional changes have also been observed in organic–inorganic hybrid HP nanocrystals. Analogous to CsPbBr₃, the NCs \rightarrow

102

NPs transformation, bandgap blue-shift, PL enhancement, and carrier lifetime shortening were also demonstrated in decompressed MAPbBr₃ nanomaterials (Fig. 9k–l) [82].

Understanding the effectivity of pressure treatment, namely the tunability of structure and properties in materials after compression-decompression cycle, is crucial for future practical exploration. Using a combination of structural and optical characterizations, as well as DFT simulations in a series of 2D (C₄H₉- $NH_{3}_{2}(CH_{3}NH_{3})_{n-1}Pb_{n}I_{3n+1}$ (*n* = 1,2,3,4) perovskites, a new mechanism was proposed to reveal the origin of effective pressure treatment, in which achieving metastable states with very long relaxation time through compression-decompression cycle is critical [90]. From a thermodynamic viewpoint, the achieved metastable states at ambient conditions must have similar energies to the ground state, while there must be an obvious difference in structural parameters, such as Pb-I-Pb bond length/ angle. Thus, property improvement/modification can be expected. Such a requirement cannot be easily realized in some HPs, such as $(C_4H_9NH_3)_2(CH_3NH_3)Pb_2I_7$ (*n* = 2) and $(C_4H_9 NH_3)_2(CH_3NH_3)_2Pb_3I_{10}$ (*n* = 3), due to their flattened energy profile, but are not favored in $(C_4H_9NH_3)_2PbI_4$ (*n* = 1) with its deep energy well. The pressure-treated (C₄H₉NH₃)₂(CH₃NH₃)₂Pb₃I₁₀ (n = 3) with metastable states shows enduring bandgap narrowing by 8.25% with stability under ambient conditions, while there are no tunable properties observed in (C4H9NH3)2PbI4 (n = 1) after the same pressure treatments. This proposed mechanism is derived from a basic energy viewpoint and helps us establish a phenomenological model about the tunability of material properties by pressure treatment in HPs.

Novel properties at high pressures

High pressure has unlocked the door of a new HP material world, where wholly new properties that do not exist at ambient conditions have been discovered, including bandgap nature transition [69], metallization [54,86], giant phonon tuning effect [81], topological properties [121], and enhanced ferroelectricity [88].

In 2016, Wang et al. reported the bandgap nature of MAPbI₃ at ambient conditions is indirect and 60 meV lower than the direct bandgap transition [69]. Also, the CBM is believed to be slightly shifted in k-space with respect to the VBM. They attributed this behavior to the Rashba-splitting of the conduction band from the spin–orbit coupling. They discovered an indirect-direct bandgap transition at mild pressure, ca. 0.325 GPa due to the reduction in the local electric field across the Pb atom and weaker Rashba-splitting (Fig. 10a–c). Their discoveries are consistent with the results reported by Hutter et al. and have been employed to understand the electron–hole recombination behavior in HPs [122].

Pressure-driven metallization in HPs is another unusual phenomenon. In 2017, Jaffe et al. measured the bandgap and absorption/reflection behavior of MAPbI₃ through visible and mid-IR spectroscopy up to 64 GPa (Fig. 10d–e). A decreasing trend in the bandgap after 6 GPa and Drude-like modes at low frequency at 60 and 64 GPa was observed, suggesting metallic behavior in this highly disordered material [54]. This semiconductor–metal transition in MAPbI₃ was later confirmed by the measured temperature dependence of conductivity at various pressures (Fig. 10f). The pressure-driven metallization was then suggested

RESEARCH: Review



FIGURE 9

Ambient properties of HPs after effective pressure treatments. (a) Narrowed bandgap in a decompressed FAPbl₃ sample after the applied pressure is totally removed. (b) Summary of bandgaps of $(BA)_2Pbl_4$ (1/n = 1), $(BA)_2MAPb_2l_7$ (1/n = 0.5), $(BA)_2(MA)_2Pb_3l_{10}$ (1/n = 0.33), $(BA)_2(MA)_3Pb_4l_{13}$ (1/n = 0.25), and MAPbl₃ (1/n = 0) before compression and after decompression. (c)–(e) Enhanced electrical conductivity in MASnl₃ after a compression–decompression cycle. (f) and (g) Representative TEM images and schematic illustrations (inset) of the CsPbBr₃ nanocrystals and pressure-sintered 2D nanoplatelets. (h) Schematic process of the pressure-sintering process of CsPbBr₃. (i) Enhanced PL and prolonged carrier recombination lifetime in pressure-sintered CsPbBr₃ 2D nanoplatelets. (g) and (k) Bandgap blue-shift and carrier lifetime shortening in the pressure-synthesized MAPbBr₃ NPs compared to the original nanocrystals. Revised from [46,57,61,82], and [90] with permission.

in Cs₃Bi₂I₉ by *in situ* electrical resistance measurements [86]. These measurements provide crucial information about the new electronic properties and introduce exciting questions, such as whether there is superconductivity in HPs and whether the superconductivity, if present, can be induced by pressure or strain.

By inelastic neutron scattering measurements, pressure-driven polar rotation and the resulting giant phonon tuning effect have been revealed in MAPbI₃ by Wang et al. [81]. They attributed it to the rotation of the organic cations and rotor–phonon coupling, which controls the behavior of the phonon and thermal properties. A similar rotor-dominated mechanism has been reported in carrier recombination properties via electron–rotor interaction.

Some theoretical works also propose novel properties may exist in compressed HPs, although further experimental confirmations are required. By first-principles calculations, Liu et al. concluded the first example of ferroelectric and topological orders coexisting in cubic CsPbI₃ [121], which is attributed to



FIGURE 10

Pressure-induced novel properties in HPs. (a)–(c) Pressure-induced Indirect–direct bandgap transition in MAPbl₃. (d)–(f) Pressure-induced metallization in MAPbl₃. (g)–(i) Applications of pressure-induced ferroelectric topological insulators. Revised from [54,69], and [121] with permission.

the suppression of the Pb–I framework rotation. The ferroelectric topological insulator may find applications in ferroelectricity stabilizers (Fig. 10g), ferroelectric domain wall-based Veselago lenses (Fig. 10h), and nanoscale topological p–n junction arrays (Fig. 10i). In addition, the pressure-driven ferroelectric enhancement and direct–indirect bandgap transition in CsPbI₃ were suggested via *Ab initio* simulations [88]. The pressure-driven ferroelectric enhancement has been previously predicted in classic ferroelectrics PbTiO₃ by first-principles calculations [123], where the huge dielectric and piezoelectric constants are comparable to relaxor-PbTiO₃ solid solutions with MPB compositions [124,125]. These expectations need further experimental evidence and high-pressure measurements of ferroelectric properties, such as the *P–E* loop and temperature dependence of permittivity.

Perspective

Tremendous progress has been made in the past few years in obtaining and understanding the unique properties of photo-

voltaic HPs under pressures. In conclusion, we have witnessed that pressure dramatically changes a diverse range of properties in HPs, such as their crystal phase, lattice parameters, order and disorder, Raman/IR vibration, phonon, optical bandgap, carrier dynamics, electrical/dielectric performance, and ferroelectricity, which are of fundamentally important for future optoelectronic and other energy-related applications.

Thus, the term "pressure engineering" can be developed to describe the processing of effective modifications and improvements by pressure treatments, including hydrostatic/non-hydrostatic compression and artificial stress. There is a commonality between pressure engineering and previously well-known doping engineering: doping is a kind of chemical pressure, or pressure is continuous doping [126]. The generating lattice-mismatch in HP-based thin films for device performance enhancement also belongs to pressure engineering since high stress on the order of GPa is possible from the high level of mismatch, which has been convinced in ferroelectric perovskites, such as $BaTiO_3$ and $SrTiO_3$ [127,128]. Research activities in pressure engineering on HPs have been primarily driven by the search for better energy materials' enhanced and tunable properties, and the understanding of the structure–property relationship from a new thermodynamic dimension. In the future, challenges remain, and we may expect the following:

"Negative pressure effects"

Tinte and co-workers theoretically predicted the enhanced ferroelectricity in PbTiO₃ and BaTiO₃ by applying a hydrostatic tensile pressure, or so-called "negative pressure" [129]. Their hypothesis was then confirmed in the wire interiors of free-standing PbTiO₃ nanowires [130], indicating that negative pressure is a new tool to modify the structural and functional properties in HPs, especially on the nanoscale, and the opposite trends to those under hydrostatic compression can be expected.

Evolutions of organic groups in HPs upon high pressure

In contrast to the well-studied inorganic materials, limited studies have been conducted on the structural transformations of organic groups in hybrid HPs. It is essential to pay more attention to the characterizations of organic groups to draw a full picture of the high-pressure structure, and neutron scattering should be employed due to its strong sensitivity to light elements carbon, nitrogen, and hydrogen.

Characterization of pressure-induced disorder

It should be noted that most of the reported properties of highpressure structures are focused on the crystalline phase rather than the disordered or amorphous states, although some novel phenomena have been found there. The lacked investigations can be realized through high-energy X-ray tools and pair distribution function (PDF) analysis, and the results may provide clues on some open issues, such as (1) Does the structural amorphization dominate the sustaining bandgap narrowing in $Cs_2AgBiBr_6$ [58]? and (2) what is the mechanism for pressure-driven metallization in MAPbI₃ at its amorphous state? Therefore, understanding the disorder is particularly interesting for developing multi-functional devices and understanding the new properties at high pressures.

Large-volume sample preparation

Although improved ambient properties have been concluded in HPs by pressure engineering, further experimental confirmation is needed to convince the application advantages in a real photovoltaic device, which requires a large-volume sample. Diamond anvil cell technology (DAC) is usually used to generate controllable pressure at a GPa scale, and the sizes of the sample in a DAC can be as small as $10-500 \ \mu\text{m}$. A large-volume press (LVP) high-pressure facility could be promising [131,132] alternative to overcome this challenge. The LVP high-pressure facility determines physical characteristics of materials under high-pressure and temperature conditions, using a large-volume device with thousands of tons of force. LVP helps us to obtain the pressurized samples above millimeter scale size, which is enough for a solar cell device.

Pressure engineering tailors perovskite properties for better performance, such as PCE. To date, there is no report on *in situ* high-pressure solar cells devices, nor any device made from the pressure-treated HP materials. However, breakthroughs are expected in the future. We have witnessed the simultaneous band-gap narrowing and carrier-lifetime prolongation in MAPbI₃ and FAPbI₃ at very mild pressures, indicating the stronger light absorbance together with greater photovoltage, respectively, which are conducive to higher PCE. There is still a long way to go to achieve a better functional device from pressure engineering and pressure. The pressure dependence defect and carrier dynamics, high-pressure quenching technique [134], and design and ultra-precision machining of diamond anvils should be focused on to achieve this goal.

In short, in future high-pressure research on HPs, we look forward to (1) Clarifying the structure–property relationship in a comprehensive manner and correlating the optimum and environmentally stable materials properties with detailed structural information; (2) Discovering novel and unprecedented properties that have never been found in photovoltaic perovskites to allow next-generation materials by design; and (3) Obtaining improved materials with enhanced and retainable functionalities for practical photovoltaic applications.

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Appendix A. Supplementary data

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