

Pressure-induced Effects in Organic-Inorganic Hybrid Perovskites

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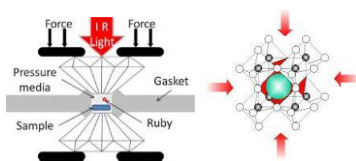
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ABSTRACT

In this perspective it is provided an overview of the pressure-induced effects on hybrid organic-inorganic perovskite for photovoltaics applications. It is shown that a fine-tuning of the most relevant photovoltaic properties, including band gap and carrier lifetime, is indeed possible by applying pressure over a rather small range and that such phenomena closely correlate with pressure-induced structural changes. High-pressure research can be used to search for new materials since the high-pressure structural configuration can be used as a model for tailoring ambient pressure compounds under proper chemical substitution, and the band-gap tuning and enhancement of carrier lifetime with applied pressures can be a guide to design new hybrid perovskites with desired optical properties as a function of structural parameters.

TOC GRAPHICS



The spectacular photovoltaic properties of organic–inorganic hybrid perovskites, such as the long diffusion length, the largely tunable bandgap and the high absorption coefficients, qualify them as outstanding materials for a variety of technological applications.¹⁻³ Moreover, the combination of low fabrication costs with a high and fast-growing power conversion efficiency (PCE, more than 22%) makes these perovskites extremely attracting within the emerging materials for solar cells. The most popular lead halide perovskites APbX₃ (X a halogen like Cl, Br, I) consist of a 3D network of corner sharing PbX₆ octahedrons with the A organic cation filling the 12-fold cubo-octahedral voids. The occupancy of the A-site by an organic molecule, instead of a single ion, gives the system further degrees of freedom and potential variability. The large variability in chemical composition and in size and shape of the organic component is at the origin of the versatility of these systems and of the large tunability of their properties. Methylammonium (MA) [CH₃NH₃⁺] is the most commonly used organic cation, although, very recently, better performances have been obtained with Formamidinium (FA) [HC(NH₂)₂⁺].³ Depending on the relative size/shape of the organic cation to the voids within the cage of the octahedra, it can freely rotate or be locked in a specific orientation. To this respect, the strength and the extension of the H-bond network (*i.e.* mainly N-H-X bonds) are the parameters governing the microscopic dynamics of the cation at the A-site. Although it is well established that the electronic band structure is mainly governed by the inorganic part, it is clear that the organic cation, through the interaction with the twelve surroundings halogens, affects the inorganic skeleton and, in turn, the optical properties.¹⁻³ The complex interplay between the organic and the inorganic part is indeed still largely unknown and unexplored. The interaction among the organic part is mediated by the inorganic lattice and this, in turn, is modified by the dynamics and/or the orientation of the organic cation. At high temperatures, the organic cation finds itself in a sort of *liquid-state* where the

molecule freely rotates in the voids of the cubic perovskite lattice, whereas on decreasing temperature the molecules lock in an ordered orientational configuration within a lower symmetry (*e.g.* tetragonal or orthorhombic) inorganic lattice. This pattern of transitions is observed in different lead halide perovskites as a function of temperature, the MAPbBr₃ being prototypical in this respect. It has been very recently demonstrated that the state of the A-site ion has a really strong effect on the carrier lifetimes and diffusion lengths that are comparable with those of high purity semiconductor single crystals, despite the modest charge carrier mobilities and the presence of defects (films are often prepared under comparatively basic conditions).⁴

Within this framework, it is clear that a tool that allows studying the system by finely tuning the organic-inorganic interaction, can be of paramount relevance to understand property tuning and provides a significant opportunity for tailoring combined functionality within a single material. While studies of temperature-dependence ordering and hydrogen bonding of the organic cations exist, the knowledge of pressure-induced effects on hybrid perovskites and specifically on the organic-inorganic interaction and its structure remains scarce.

As a matter of fact, the high-pressure (HP) investigation of hybrid perovskites is relatively recent and mainly focused on methylammonium lead iodide hybrid perovskite (MAPbI₃). From the end of 2015, seven distinct papers considered the role of pressure on MAPbI₃.⁵⁻¹¹ These works firstly addressed the evolution of the crystal structure with pressure which is prerequisite in order to correlate and understand the pressure-induced changes of functional properties.⁵⁻¹¹ Refs. 5, 6, 8, 9 performed HP powder X-ray diffraction (PXRD) while ref. 7 also included single-crystal x-ray diffraction (SCXRD) data at 0 GPa and 0.3 GPa.⁷ Finally, refs. 10 and 11 focused on SCXRD with data points at 0 and 0.4 GPa for ref. 10 and at 0, 0.30, 0.45, 2.34 and 2.71 GPa for ref. 11.

The ambient temperature and pressure crystal structure of MAPbI₃ is tetragonal (space group, s.g., *I4/mcm*) with average lattice parameters of $a=b= 8.70-8.90 \text{ \AA}$ and $c=12.64-12.68 \text{ \AA}$. Although the crystal structure of MAPbI₃ is relatively simple, there has been a significant disagreement regarding the structural evolution of the lattice with pressure among the published papers.⁵⁻¹¹ All of them agree with the presence of a phase transition around 0.3-0.4 GPa except for ref. 6 reporting a higher transition pressure of about 0.6 GPa. The latter, however, together with ref. 8, carried out the HP XRD experiments without any hydrostatic pressure transmission medium. The most significant inconsistency among the reported HP data on MAPbI₃ is however related to the nature of the novel phase occurring above 0.3-0.4 GPa. Most of the PXRD studies and the SCXRD work by Jaffe and co-workers suggested a transition towards a more distorted orthorhombic structure (*Imm2* s.g.).⁷ More accurate single-crystal diffraction experiments, such as those reported by Szafranski and Katrusiak, could finally determine that the high-pressure phase of MAPbI₃, found at about 0.3 GPa, has a cubic symmetry with *Im-3* space group.¹¹ The Authors of ref. 11 give a very solid argumentation from their SCXRD patterns analysis, providing a definite and authoritative interpretation of the crystal structure evolution of MAPbI₃ with pressure and indicating also that crystal twinning can lead to misinterpreted data.¹¹ In particular, Szafranski and Katrusiak, determined the presence of only one phase transition from the ambient pressure tetragonal structure (*I4/mcm*, defined as phase II in ref. 11 and Figure 1 below) to the cubic high-pressure polymorph (*Im-3*) at about 0.35 GPa (defined as phase IV in ref. 11 and Fig. 1)) and excluding the presence of an orthorhombic high-pressure structure.¹¹ This result is of key importance for the interpretation of the changes observed in the optical properties as a function of pressure, as it will be shown later in the text. A sketch of the ambient pressure tetragonal and high-

pressure cubic structures are reported in Figures 1a and 1b, respectively. Figure 1c shows the evolution of the cell volume with pressure.

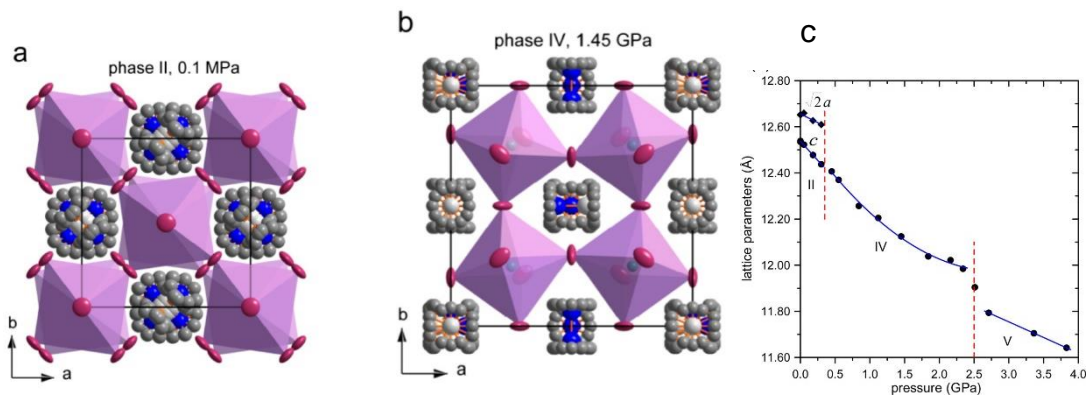


Figure 1. Crystal structures of MAPbI_3 phases at 0.1 MPa (a) and at 1.45 GPa (b). (c) Lattice parameters evolution with pressure. Reprinted from ref. 11 (American Chemical Society 2016).

One important structural difference between the tetragonal and cubic phases, which has profound implications on the optical properties, is the increased disordering of MA cations by crossing the phase transition within the two possible voids created by the $Im-3$ symmetry.¹¹ On further increasing pressure, the authors of ref. 11, observed a discontinuity in the cubic lattice parameter at about 2.7 GPa (Figure 1(c)). At this pressure, the crystal structure (named V in ref. 11 and in Figure 1) can be still indexed with the cubic $Im-3$ space group and this transition is associated with a strong strain and a considerable pressure hysteresis as well as amorphization of the sample. Previous powder diffraction data misinterpreted this transition due to the possible coexistence of the two high pressure cubic phases with $Im-3$ space group and different lattice parameters.⁷

Another interesting feature observed by further increasing pressure is the progressive amorphization of MAPbI₃ which starts around 3 GPa and is completed close to 4 GPa, as it is shown in Figure 2.^{7,9}

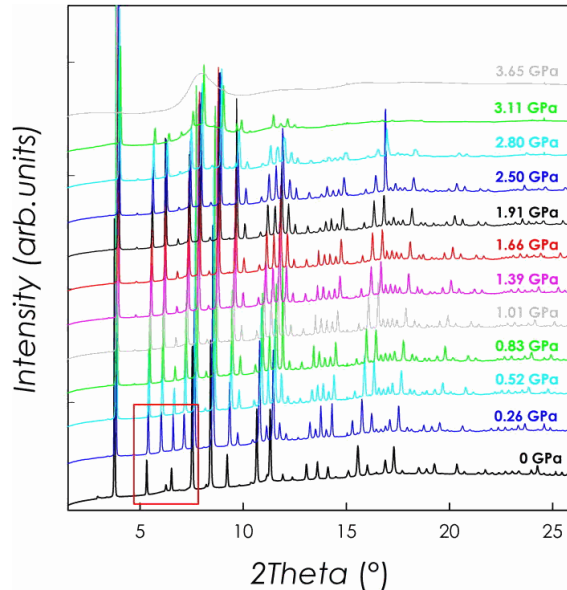


Figure 2. Crystal HP XRD patterns for the MAPbI₃ perovskite. Red box highlights a representative region where the phase transition occurs. Reprinted with permission from Ref. 9 (American Institute of Physics 2016)

The pressure-dependence of the amorphization phenomena seems to be closely related to the hydrostatic conditions used during the experiments. When no pressure transmitting medium is used, for example, the pressure where a full amorphous phase is observed was reported to be close to 20 GPa.⁶ Also, in ref. 7, Bragg peaks are found up to 50 GPa and only ref. 9 could report the achievement of a full amorphous phase close to 4 GPa. High-pressure data at 2.7 GPa on single crystals confirm the reduction of the average order of the cubic *Im-3* structure and provide a detailed explanation of such phenomena which is related to the disorder of the cations expanded into the glassy state of all lattice.¹¹ One peculiar aspect of MAPbI₃ is that the amorphization is

triggered by an isostructural phase transition and occurs suddenly at the transition point and then proceeds gradually with increasing pressure.¹¹

Finally, from this amorphous phase it is possible to recover, during decompression, a full crystalline phase of MAPbI₃ even in experiments where very high pressures (>40 GPa) are reached.^{6,7,9} The crystal structure at ambient pressure of the recovered phase after decompression was as well object of different and conflicting interpretations. In general, it has been reported that MAPbI₃ recovers the tetragonal ambient pressure phase after decompression while in ref. 9 it is the high pressure phase which is stabilized after pressure release.⁵⁻¹¹ Irrespective to the exact nature of the crystal structure recovered after compression, it is of significant relevance that such a “soft” material could completely re-crystallize in a fully ordered lattice after being amorphized.

From this overview about the HP structural investigation on MAPI it is clear that the data spread comes probably not only from the conditions used during the experiments but also from samples' quality in terms of grain size, morphology and chemical synthesis.⁹ It is possible to provide some guidelines for further HP structural studies on hybrid perovskites: i) use of proper hydrostatic conditions; ii) where possible, the investigations should be performed on well-characterized single-crystals; and iii) properly define the nature of the powdered samples in terms of morphology and preparation method.

In parallel with the structural studies, all the above reported papers investigated the pressure dependence of the optical properties of MAPbI₃.

The measurement of the vis-NIR spectra of MAPbI₃ in a DAC cell revealed significant shifts by applying pressure and across the phase transitions. A first red shift of about 0.025-0.030 eV from the ambient-pressure value is observed in most of the reported studies by increasing P up

to about 0.35 GPa, *i.e.*, in the tetragonal phase and before the transition to the cubic high-pressure polymorph (*Im-3*).^{7,8,10,11} The absolute value of the ambient-pressure band-gap of MAPbI₃ is scattered between 1.50 and 1.62 eV, according to the measurement method, but the relative E_g change of ca. 0.025-0.030 eV in the ~0-0.35 GPa range is consistent among different papers.^{7,8,10,11} The decrease in the band-gap value in the tetragonal phase has been ascribed to the shortening of the Pb-I bond length which enhances the Pb *s* and I *p* orbitals coupling and pushes up the VBM (Valence Band Maximum) as determined from first-principles calculations.¹⁰ At the transition from the tetragonal to the cubic symmetry (~0.35 GPa) the E_g has a “blue jump” of about 0.06 eV with a slight increase up to 1 GPa followed by a decrease up to the next transition pressure of about 2.5 GPa.^{7,8,10,11} At this pressure the band-gap abruptly widens again reaching a value of about 1.8 eV around 3.5-4 GPa.^{9,11} When the sample is in the amorphous phase, the photoluminescence signal completely changes and a large, weak peak, apparently centred at even higher energy, appears.⁹ The trend of the E_g variation with pressure and visual change of the sample within the DAC are reported in Figures 3a and 3b, respectively.

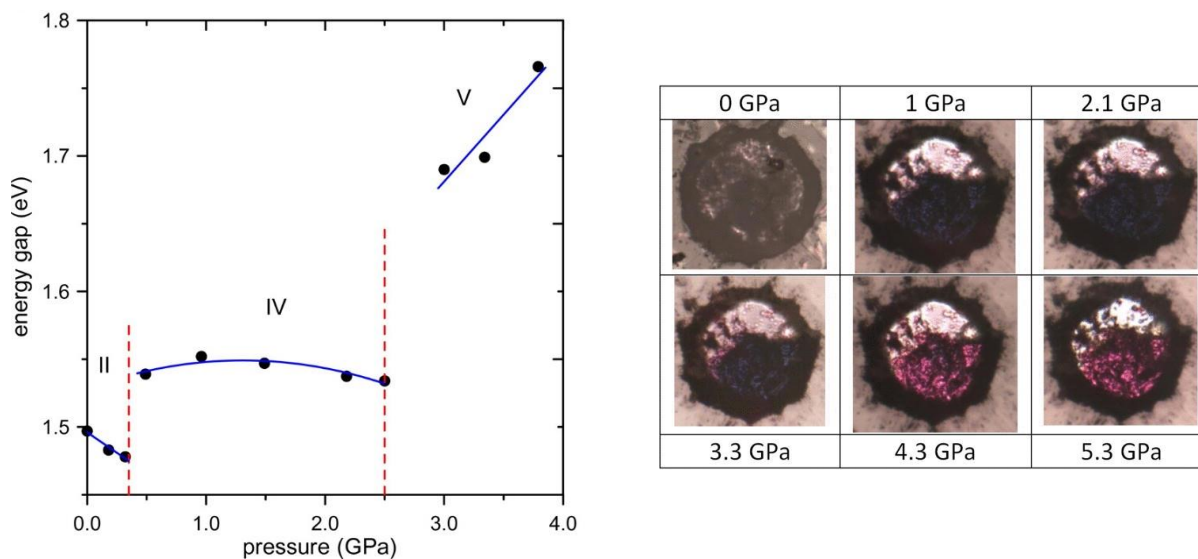


Figure 3. a) Pressure dependence of the optical energy gap of MAPbI₃; b) Micro-photographs of MAPbI₃ inside the DAC at different pressure values. Reprinted from ref. 11 (American Chemical Society 2016) and Reprinted with permission from Ref. 9 (American Institute of Physics 2016).

The main origin of the blue-shift observed above ca. 3 GPa has been correlated to the peculiar structural features of the high-pressure *Im-3* phase (named as phase V in ref. 11) and to the distortion of the (PbI₃)_n framework and its frustration, induced by strongly interacting cations trapped at random orientation in the squeezed voids of the structure.¹¹ Such distortion results in band-gap variations with pressure much larger than those observed at ambient pressure as a function of temperature. One intriguing aspect of the high-pressure behaviour of MAPbI₃ is the local-symmetry breaking while the average crystal symmetry is maintained, which nucleates the amorphization at the phase transition. Such behaviour and its microscopic nature is worth of further investigation.

Kong and co-workers measured the time resolved photoluminescence on MAPbI₃ single crystals and polycrystalline samples as a function of pressure in order to determine the influence

of pressure on the carrier lifetime (τ), which is a key property influencing the photovoltaics properties.¹⁰ For both samples, it was observed a significant enhancement of τ by increasing pressure, with a peak value at about 0.3 GPa, *i.e.* at the $I4/mcm \rightarrow Im-3$ phase transition. In particular, by considering the relative contribution of slow and fast components, the mean carrier lifetime $\langle\tau\rangle$ increases by 70% and 100% in single-crystal and polycrystalline samples, respectively, at 0.3 GPa.¹⁰ This trend, shown in Figure 4, was explained by considering that, as pressure increases, the trap states that are already present in the subgap close to VBM become even more shallower. Thus, a large portion of recombination becomes radiative, and a longer carrier lifetime is consequently expected.¹⁰

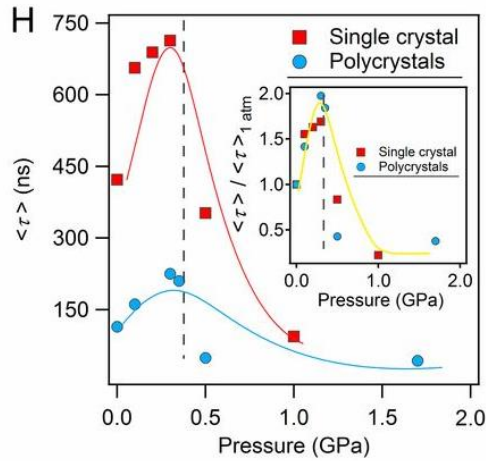


Figure 4. Pressure dependence of the mean carrier lifetime, for both MAPbI₃ single-crystal and polycrystal samples. Peak values in carrier lifetimes of MAPbI₃ were observed at 0.3 GPa. (*Inset*) Normalized results compared with the values of $\langle\tau\rangle$ measured at ambient pressure. Reprinted with permission from Ref. 10 (American Institute of Physics 2016).

Such enhancement of carrier lifetime, observed also in other systems as a function of applied pressure (see later in the text), could be further explored in materials' design in order to enhance the photovoltaics properties.

Among the MA-based lead trihalides, MAPbBr₃ and MAPbCl₃ have been as well investigated by means of high-pressure techniques concerning both the structural and optical properties.^{7,10,12,13,14}

Concerning the MAPbBr₃, a first investigation by Swainson and co-authors addressed the structural evolution of a fully deuterated sample by means of high-pressure neutron diffraction up to 3 GPa employing a Paris-Edinburgh cell and 2-propanol as pressure transmitting medium.¹² This work was published in 2007, well before the discovery of exceptional photovoltaics properties by hybrid perovskites. Main result of this work was the observation of a phase transition from the room temperature cubic structure of MAPbBr₃ (*Pm-3m*) to a high-pressure *Im-3* cubic phase at about 1 GPa. The authors did not observe any further structural transition before amorphization which occurred above ~2.8 GPa but suggested the existence of an orthorhombic *Pnma* phase under compression.⁸ Interestingly, the authors of this work also pressured the cell at 2.4 and 3.2 GPa and then cooled them to 100 K, well below the temperature at which the orthorhombic *Pnma* phase is entered at ambient pressure.^{15,16} At both pressures, the sample remained in the *Im-3* cubic phase and slowly amorphized on cooling at the higher pressure.¹² Their conclusion is that the sample amorphized prior to the organic cations undergoing long-range orientational ordering in the *Pnma* phase.¹² In a more recent work by Wang and co-workers, carried out by means of HP-XRD in a DAC up to 34 GPa, the same *Pm-3m* → *Im-3* phase transition reported in ref. 12 was observed at a similar pressure.¹³ A smaller transition pressure has been reported in ref. 10 (about 0.5 GPa). However, in addition to this transition, a second phase transformation from *Im-3* to *Pnma* was reported to be present starting from 1.8 GPa.¹³ The integrated 1D XRD profiles for MAPbBr₃ and the evolution of the lattice volume taken from ref. 13 are reported in Figures 5a and 5b. Phases I, II and III in Figure 5b refer to *Pm-3m*, *Im-3* and *Pnma*, respectively.¹³

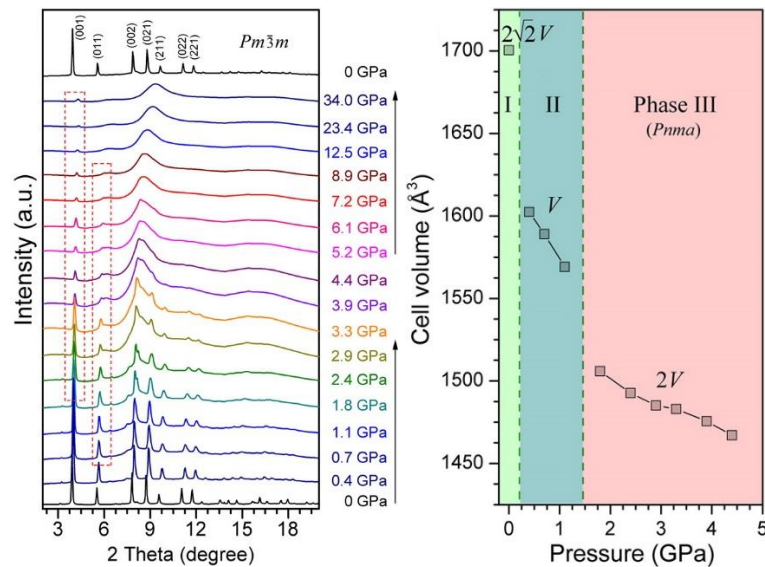


Figure 5. a) Synchrotron XRD pattern of MAPbBr₃ during compression up to 34 GPa and decompression (top pattern); b) Cell volume evolution of MAPbBr₃ as a function of pressure at room temperature. Reprinted with permission from ref. 13 (American Chemical Society 2015).

As can be seen from Figures 5a and 5b, amorphization of MAPbBr₃ starts above 2 GPa and the sample is nearly fully amorphous at the highest pressure investigated (34 GPa).¹³ Interestingly, persistence of the main peak (001 reflection) is observed even at 34 GPa and, after decompression, the sample is fully crystalline and recovers the starting *Pm*-3*m* cubic symmetry, with an analogous behaviour as observed for the MAPbI₃ perovskite. The fact that the (001) peak remains present even at very high pressures, together with the persistence of the (001) reflection up to about 9 GPa, which are both related to the long-range ordered packing of heavy atoms Pb and Br, suggests that the amorphous material retains the cross-linking PbBr₆ perovskite skeleton but with highly distorted MA molecules, as also suggested from the single crystal study on MAPbI₃.^{11,13}

The study of the photovoltaic related properties on MAPbBr₃ has been carried out by means of photoluminescence (PL) spectroscopy as a function of pressure in a DAC. An anomalous peak shift was observed upon compression: first a gradual red shift in the 0-1 GPa region followed by a blue shift above 1 GPa.¹³ It is thought that the abnormal PL/band gap evolution is due to the competition of the compression effect to shorten the bonding length and pressure-induced amorphization to break certain bonds. Figures 6a and 6b report the photoluminescence spectra of MAPbBr₃ (acquired with a 325 nm laser) as a function of pressure and the derived band-gap trend.

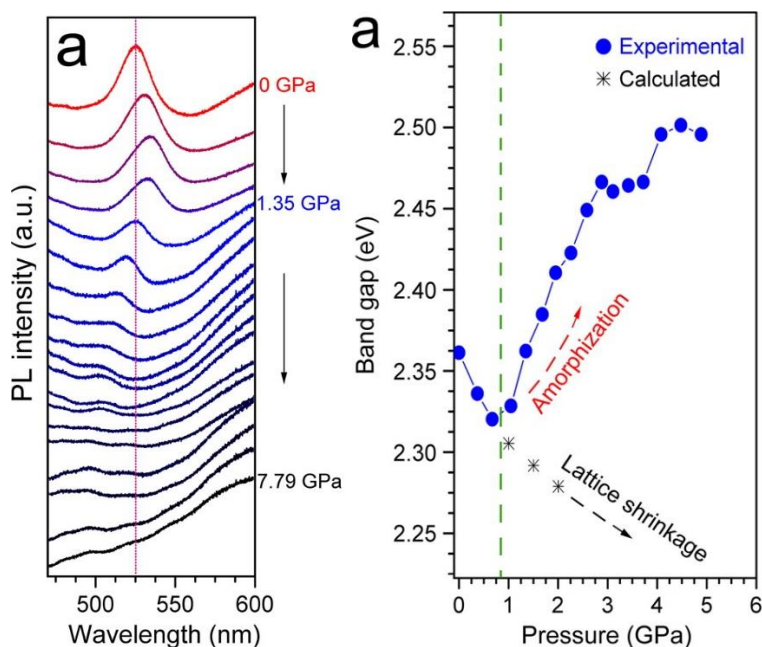


Figure 6. a) Room temperature photoluminescence spectra of MAPbBr₃ as a function of pressure during compression; b) Derived band-gaps of MAPbBr₃ as a function of pressure. Reprinted with permission from ref. 13 (American Chemical Society 2015).

As can be seen from Figure 6b, the variation of the band-gap is of about 0.2 eV in the 0-5 GPa interval, which suggests the potential use of hydrostatic pressure as a tuning medium in photovoltaics applications. The authors of ref. 13 also provided a first-principles calculation on the

partial density of states (PDOS) and on the evolution of the band-gap under pressure. Main conclusion of this investigation is that the band-gap narrowing is mainly due to the shrinkage of the PbBr_6 octahedra without a significant contribution from the MA cations, while the blue-shift is due to the pressure-induced amorphization.¹³ Another relevant result reported in ref. 13 is the observation of a considerable photocurrent up to 30 GPa for MAPbBr_3 , *i.e.*, when the material is in an amorphous phase. Again, this is a proof of the retention of a certain degree of short-range order of the perovskite phase even at very high pressures.

Just one paper reports the pressure response of the MAPbCl_3 hybrid perovskite.¹⁴ As for the above studies on similar systems, a combination of XRD, Raman, optical absorption and photoluminescence measurements under pressure have been collected.

HP-XRD on MAPbCl_3 revealed the presence of two phase transformations, in particular a cubic to cubic ($Pm-3m \rightarrow Pm-3m$) transition at about 0.8 GPa, and a cubic to orthorhombic transition ($Pm-3m \rightarrow Pnma$) at about 2.0 GPa, followed by amorphization and full recovery of the cubic symmetry after decompression from 20 GPa.¹⁴ Evolution of the lattice volume *vs.* P is reported in Figure 7a.

High-pressure Raman investigation showed that the first cubic to cubic isostructural transition mainly relies on rotation of the MA cation, as also observed for the MAPbI_3 material, while the second transition is mainly related to the tilting distortion of the $[\text{PbCl}_6]^{4-}$ octahedra.^{11,14} The pressure induced amorphization of MAPbCl_3 retains its tilting distortion of the $[\text{PbCl}_6]^{4-}$ octahedra inorganic perovskite skeleton but with highly distorted MA organic molecules, again in close analogy with MAPbI_3 .^{11,14}

The PL spectra under pressure allowed determining the variation of the band-gap as a function of pressure, as shown in Figure 7b.¹⁴

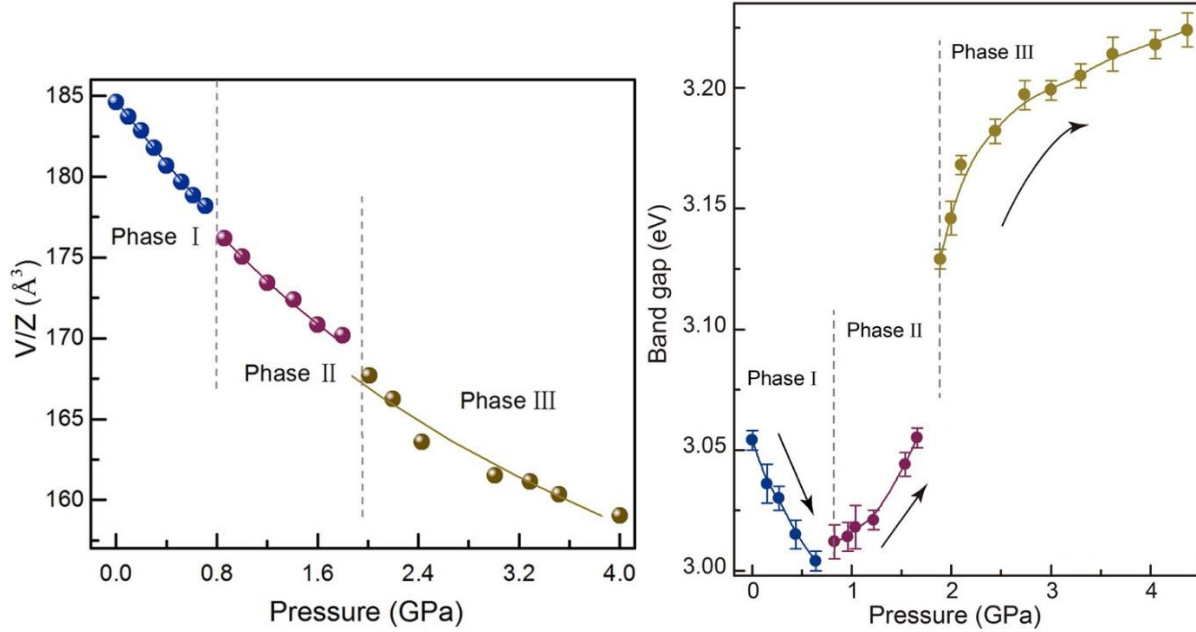


Figure 7. a) Pressure dependence of the unit cell volume of MAPbCl₃; b) Derived band-gap of MAPbCl₃ as a function of pressure during compression together with the crystal structures observed in the various P -ranges. Reprinted with permission from ref. 14 (American Chemical Society 2015).

As can be appreciated from Figure 7b, the band-gap first experiences a gradual red-shift within 0-0.8 GPa, followed by a blue-shift from 0.8 GPa up to 1.9 GPa, *i.e.*, at the cubic to cubic phase transition. At around 1.9 GPa, a new absorption edge appears in the PL spectra leading to a “blue jump” which continuously shifts until becoming very weak close to the pressure-induced amorphization. The results of Figure 7b demonstrate that the band-gap of MAPbCl₃ can be finely tuned to the UV region by pressure, accompanied by the appearance of two turning points originating from the structural changes in the crystal. It has been suggested that when pressure is applied to the cubic phase (I) of MAPbCl₃ perovskite, the [PbCl₆]⁴⁻ octahedra contracted, thus

reducing the Pb-Cl bond length.¹⁴ This in turn enhance the coupling of the Pb-*s* and the Cl-*p* orbitals and pushed up the VBM thus leading to the observed red shift of the band-gap. In phase II, the crystal structure is still cubic but the change in the electronic state caused by the isostructural transition is responsible for the observed blue-shift.^{14, 17-19} Finally, the blue jump could be ascribed to the stabilization of the orthorhombic phase which is correlated to a deviation of the Pb-Cl-Pb bond angle from the original 180° and to a reduction of the coupling between Pb-*s* and the Cl-*p* orbitals.^{10,14} This is analogous to what happens in MAPbI₃ and MAPbBr₃ even though in presence of different crystal structures at high pressure. In any case, the blue-jump seems to be strongly related to a significant distortion of the Pb-X-Pb (X=Cl, Br, I) bond angle while continuously compressing the crystal.^{11,13,14}

Overall, the HP investigation on MA-based lead halides showed the presence of some common characteristics together with some discrepancies, in particular regarding the structural properties. All the MAPbX₃ (X=Cl, Br, and I) materials undergo structural phase transitions at relatively low pressures followed by amorphization of the sample which usually starts around 3-4 GPa without a strong dependence on the nature of the anion X. This may suggests, together with the results reported by accurate crystal structure studies performed on the hybrid perovskite samples and discussed above, that the amorphization is mainly triggered by the distortion of the MA molecules while retaining a degree of short-range order of the cross-linking PbX₆ perovskite skeleton. Such order of the perovskite skeleton might be the key feature allowing the observed restoration of a full crystalline phase after decompression from very high pressures. Further high-pressure local structure investigation is required to elucidate the microscopic characteristics of the amorphous phases found at high pressures in MA-based lead halides. Concerning the optical properties evolution with pressure, all the MAPbX₃ (X=Cl, Br, and I) perovskites undergo a first

red-shift within the fully crystalline HP phases, mainly due to the shortening of the Pb-X bond lengths, followed by a blue shift (and in some cases also a blue-jump) when entering the amorphization process which strongly distorts the Pb-X-Pb (X=Cl, Br, I) bond angles. In addition, there are clear evidences that pressure enhances the carrier lifetime in hybrid perovskites for low applied pressures, which has a significant interest for photovoltaics applications. The band-gap tuning and enhancement of carrier lifetime with (low) applied pressures may be a guide to design new hybrid perovskites with desired optical properties as a function of structural parameters.

Formamidinium (FA) based hybrid perovskites have been also object of HP investigation, even though in a more limited way compared to MA-based materials. In particular, one work addressed the HP behavior of FAPbI₃ and another one considered the FAPbBr₃ system.^{20,21}

HP-XRD on FAPbI₃ did not show any phase transition from the ambient pressure phase up to 7 GPa which is the maximum *P*-value used in ref 20 [Note: in ref. 20 the symmetry used at ambient pressure is the wrong trigonal *P3m1*, while it has been clearly demonstrated that the α -phase of FAPbI₃ (black) is *Pm-3m*].²² Again, a significant diffuse scattering is observed above 2.5 GPa which is correlated to the amorphization of the sample and significant distortion of the PbI₆ octahedra similarly to the MA-based materials.²⁰ One relevant result reported in ref. 20 for FAPbI₃, is the evolution of the optical properties with pressure. The band-gap values extracted from the HP PL spectra showed a continuous red-shift from the ambient pressure value of 1.489 eV down to 1.337 eV at 2.1 GP, which is the maximum *P*-range investigated by PL in ref. 20. Such value is of relevance since it approaches the optimal band-gap required by Shockley-Queisser efficiency limit in lead-based hybrid perovskites.²⁰ The behavior of the PL spectra for selected pressures on FAPbI₃ is reported in Figure 8, together with the extracted band-gap values.

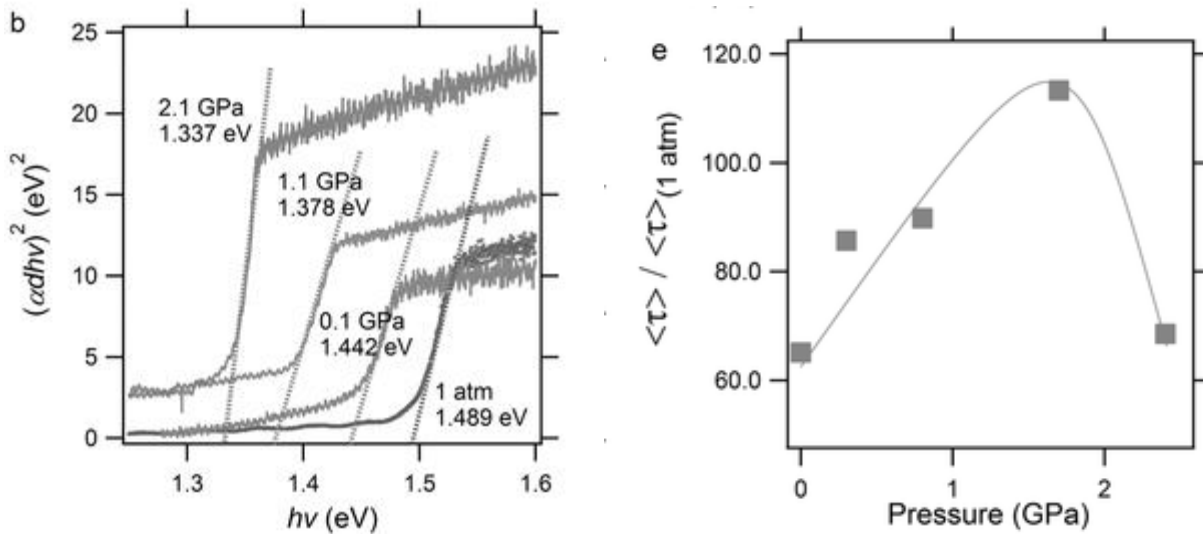


Figure 8. Direct bandgap Tauc plots of α -FAPbI₃ collected at 1 atm, 0.1 GPa, 1.1 GPa, and 2.1 GPa. Reprinted with permission from ref. 20 (Wiley Publisher 2016).

Together with this important variation of the band-gap with pressure, the authors of ref. 20 reports a concomitant significant enhancement of the carrier lifetime as a function of pressure. Figure 8b shows the variation of the normalized mean carrier lifetime (containing both the fast and low components and defined as $\langle \tau \rangle = [\alpha\tau_1/(\alpha\tau_1 + \beta\tau_2)]\tau_1 + [\beta\tau_2/(\alpha\tau_1 + \beta\tau_2)]\tau_2$) as a function of pressure. Peak values in carrier lifetimes of FAPbI₃ were observed at 1.7 GPa, where a dramatic increase in by 120% has been demonstrated, and which is mainly due to an increase of the fast component of carrier lifetime.²⁰ While the data reported in ref. 20 are of interest, some doubts may be raised regarding the samples' quality. XRD diffraction profiles showed and refined throughout the paper are, as a matter of fact, not single-phase, also considering the wrong trigonal space group used by the authors (as mentioned above). Based on this evidence, and on the fact that all the theoretical calculation have been carried out with a wrong starting structural model, most of the

correlation between the lattice variation and the electronic structure changes are questionable. In addition, the PL investigation has been limited to a too short P -range to exclude a possible blue-shift also in FAPbI_3 . Most probably, a re-evaluation of the HP measurements on FAPbI_3 is worth of being performed.

A more rigorous study has been carried out on FAPbBr_3 hybrid perovskite by HP-XRD and PL by Wang and co-workers.²¹

Figure 9a shows the evolution of the HP-XRD patterns with pressure while Figure 9b schematically shows the different crystal structures found as a function of pressure.²¹

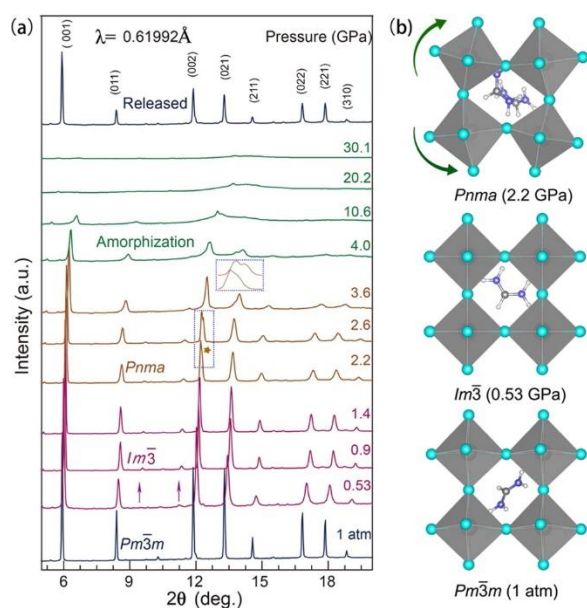


Figure 9. (a) Representative XRD patterns of FAPbBr_3 crystal at various pressure levels. Arrows mark new diffraction peaks appearing at 0.53 GPa, and the asterisk highlights the splitting of the peak at 2.2 GPa. (b) Refined crystal structures of FAPbBr_3 at ambient pressure, 0.53 and 2.2 GPa. Reprinted with permission from ref. 21 (American Chemical Society 2016).

Two phase transitions are found within 2.2 GPa, followed by amorphization above ca. 3.6 GPa and full restoration of the starting cubic crystalline phase under decompression.²¹ It is worth

mentioning that MAPbBr₃ and FAPbBr₃ crystals exhibited similar high pressure XRD behavior and the same following pressure-induced phase transition sequences: $Pm-3m \rightarrow Im-3 \rightarrow Pnma$.¹³ However, the onset of the $Pm-3m \rightarrow Im-3$ phase transition at 0.4 GPa for MAPbBr₃ was lower than the one for FAPbBr₃ at 0.53 GPa. With further compression, the second phase transition ($Im-3 \rightarrow Pnma$) occurring at 1.8 GPa for MAPbBr₃ was also lower than that of FAPbBr₃ crystal. The similar high pressure XRD behavior and the similar pressure-induced phase transition paths demonstrate that the P -induced phase transition is mainly related to [PbBr₆]⁴⁻ octahedra skeleton, and the soft organic cations simply act as templates for the [PbBr₆]⁴⁻ octahedral frameworks under pressure. However, the pressure points of two phase transitions of FAPbBr₃ are both higher than MAPbBr₃, which demonstrates that the former is less compressible under high pressure. The stabilization of the perovskite systems is another important aspect that helps to optimize photovoltaic performance.^{21,23,24}

Finally, also the trend of the band-gap values extrapolated from the HP-PL measurements on FAPbBr₃ show a similar behavior to that of MAPbBr₃, *i.e.* a first red-shift followed by a turning point and a blue-shift. The pressure dependence of the band-gap energy as a function of pressure is shown in Figure 10.

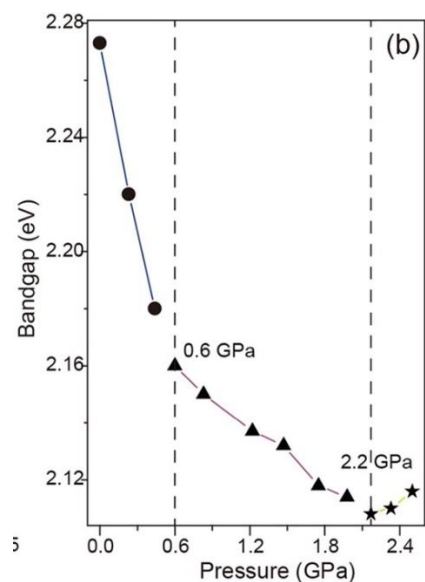


Figure 10. Pressure dependence of bandgap energy of FAPbBr₃. Reprinted with permission from ref. 21 (American Chemical Society 2016).

As can be seen in Figure 10, the rate of change in bandgap upon pressure presents two distinct turning points at 0.6 and 2.2 GPa which are most probably induced by structural changes observed at these pressures and shown in Figure 9.²¹ In particular, according to Rietveld refinements, the first transition is mainly caused by the shrinkage of the [PbBr₆]⁴⁻ octahedra, which accounts for the absorption edge and PL red-shift upon compression and the optical bandgap reduction. The abrupt blue-shift in the absorption and PL, as well as bandgap widening is induced by the tilting distortion of the [PbBr₆]⁴⁻ octahedra in the second phase transition. Finally, the Raman spectra as a function of pressure reported in ref. 21 further confirmed that the two phase transitions do not significantly affect the internal structure of the octahedra.²¹

In summary, the research carried out on hybrid perovskites has clearly shown that a significant volume compression activates a complex phenomenology involving both electronic and

structural properties. A fine-tuning of the most relevant photovoltaic properties, including band gap and carrier lifetime, is indeed possible by applying pressure over a rather small range. The microscopic origin of this pressure driven tuning is not completely understood but most of the presently available data suggest a key role of the organic-inorganic interaction that demands further investigation. Its extent and extension over the lattice can be tuned by compressing the lattice. The structural transition observed can be directly related to a pressure induced transition of the ensemble of the organic molecules from a dynamically disordered to an orientationally ordered, and finally to a statically disordered phase. The amorphous phase in the high-pressure regime still requires a deep investigation to understand its effects on the electronic properties and specifically on the carrier lifetime. High-pressure research has a recognized impact on the search for new materials since the high-pressure structural configuration can be used as a model for tailoring ambient pressure compounds under proper chemical substitution. Indeed, the band-gap tuning and enhancement of carrier lifetime with (low) applied pressures can be a guide to design new hybrid perovskites with desired optical properties as a function of structural parameters.

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