

Supporting Information

Pressure-Induced Locking of Methylammonium Cations versus Amorphization in Hybrid Lead Iodide Perovskites

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Lineshape fits of PL spectra

Figure S1 shows representative PL spectra of MAPbI₃ for different pressures to illustrate the lineshape analysis of the PL profiles. Different colors correspond to the four phases observed as a

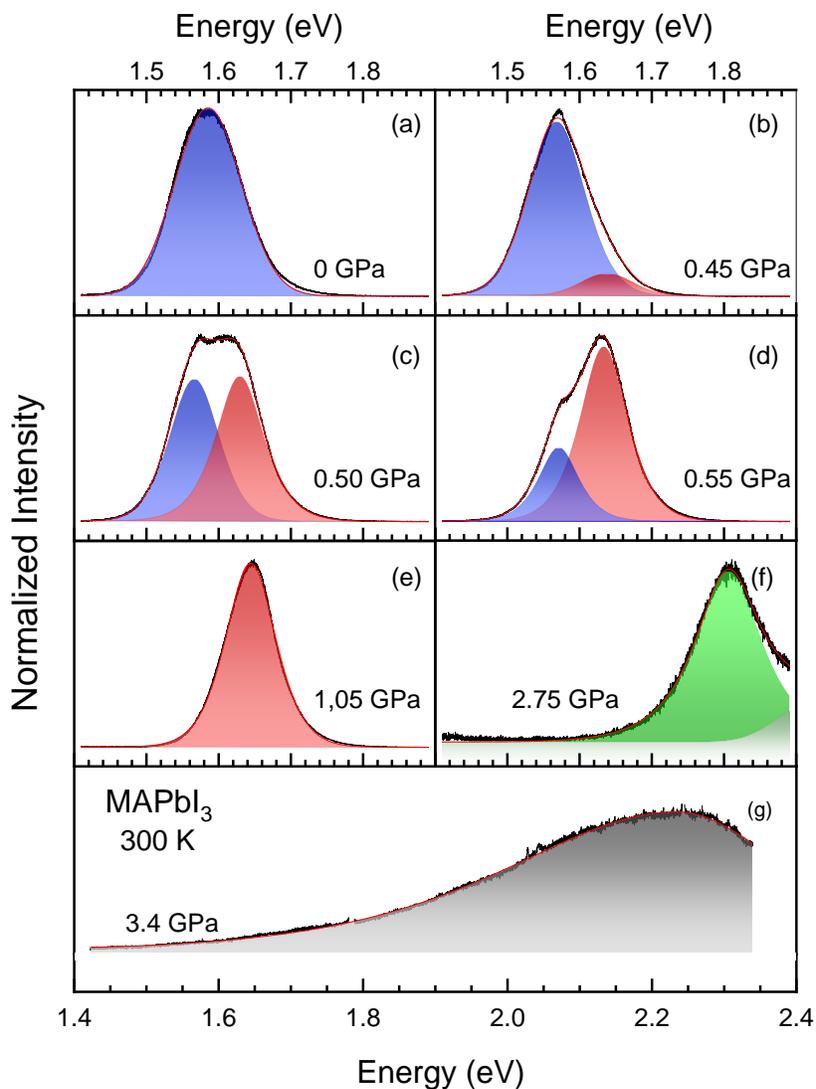


Figure S 1: PL spectra of MAPbI₃ obtained for different pressures. The spectra were normalized to their maximum intensity to ease their comparison. The different colors indicate the subsequent phases adopted by the material during the pressure upstroke (Blue: tetragonal, red: cubic, green: probably orthorhombic, grey: unknown). For pressures lower and higher than 3.4 GPa the excitation laser wavelength was 633 nm and 514 nm, respectively.

function of pressure and the same code was used throughout the manuscript. The main emission peak of MAPbI₃ at room temperature was assigned to free-exciton recombination.²⁻⁵ Thus, for the lineshape fitting of the PL spectra we used a Gaussian-Lorentzian cross-product function.¹ Its expression reads as:

$$G \times L(\hbar\omega) = A \cdot \frac{\Gamma^2}{4 \cdot s \cdot (E_0 - \hbar\omega)^2 + \Gamma^2} \cdot \exp\left(-4 \cdot \ln 2 \frac{(1-s) \cdot (E_0 - \hbar\omega)^2}{\Gamma^2}\right) \quad (1)$$

where A is the amplitude prefactor, E_0 is the peak energy position, Γ is the full width at half maximum and s is a weight parameter which takes the value $s = 0$ for pure Gaussian lineshape and $s = 1$ for pure Lorentzian. The values of these four adjustable parameters were obtained as a function of pressure from lineshape fits to the measured PL spectra using Eq. (1), as exemplified in Fig. S1. For the cases where there is a coexistence of two phases ($0.4 \text{ GPa} \leq P \leq 1.0 \text{ GPa}$) we used two cross-product functions with independent variable parameter sets.

Reversibility issues

The reversibility of the structural as well as the related pressure-induced changes in the optical and vibrational properties is certainly a matter of concern for a soft material such as MAPbI₃. Figure S2 displays Raman and PL spectra measured at two different pressures during the first pressure upstroke (black solid lines) and with decreasing pressure after reaching the highest value of the experiment (green solid lines). Whereas the Raman spectra are almost identical, the PL spectra agree well with each other, besides for small discrepancies in the peak position (probably due to small deviations in the pressure). We remark, though, that the intensity of the PL emission fully recovers after decompression. This is very important because the PL signal is very sensitive to the appearance of structural defects which usually cause its quenching. Altogether, both Raman and

PL spectra demonstrate the full reversibility of the structural changes in MAPbI₃ under hydrostatic pressure.

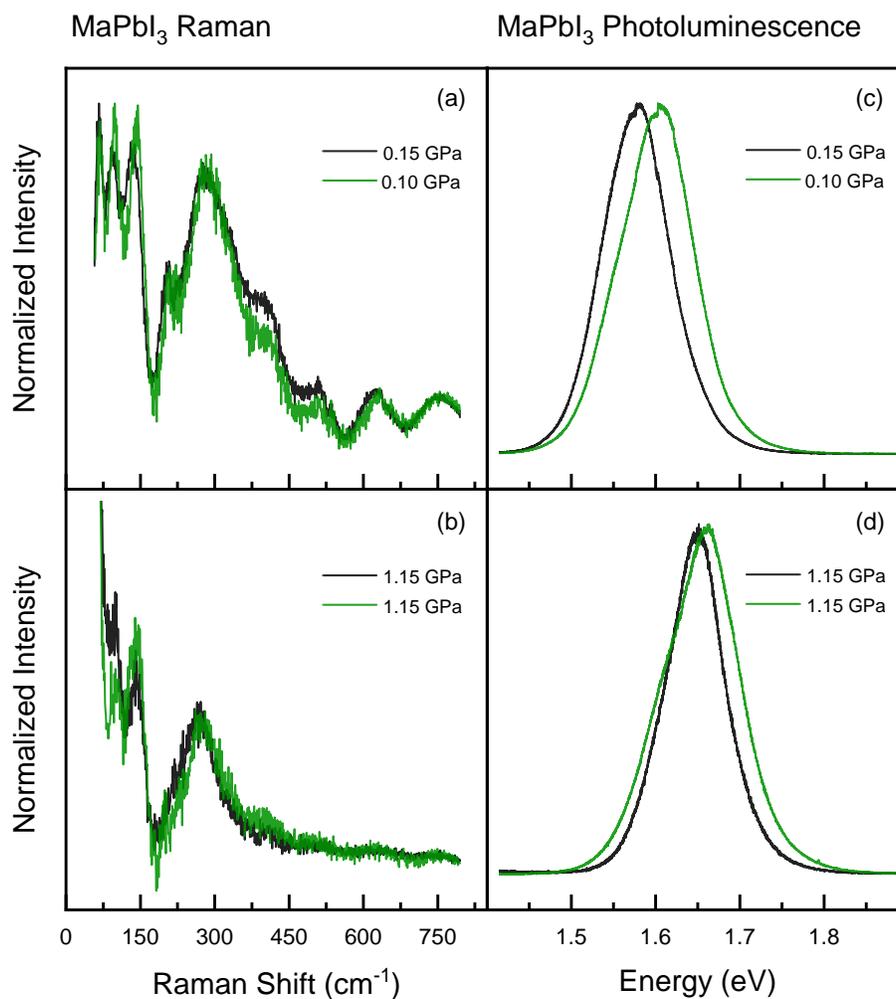


Figure S 2: (a,b) Raman and (c,d) PL spectra of MAPbI₃ obtained for the pressure upstroke (black) and subsequent downstroke (green), demonstrating the high degree of reversibility of the structural/optical changes induced by pressure.

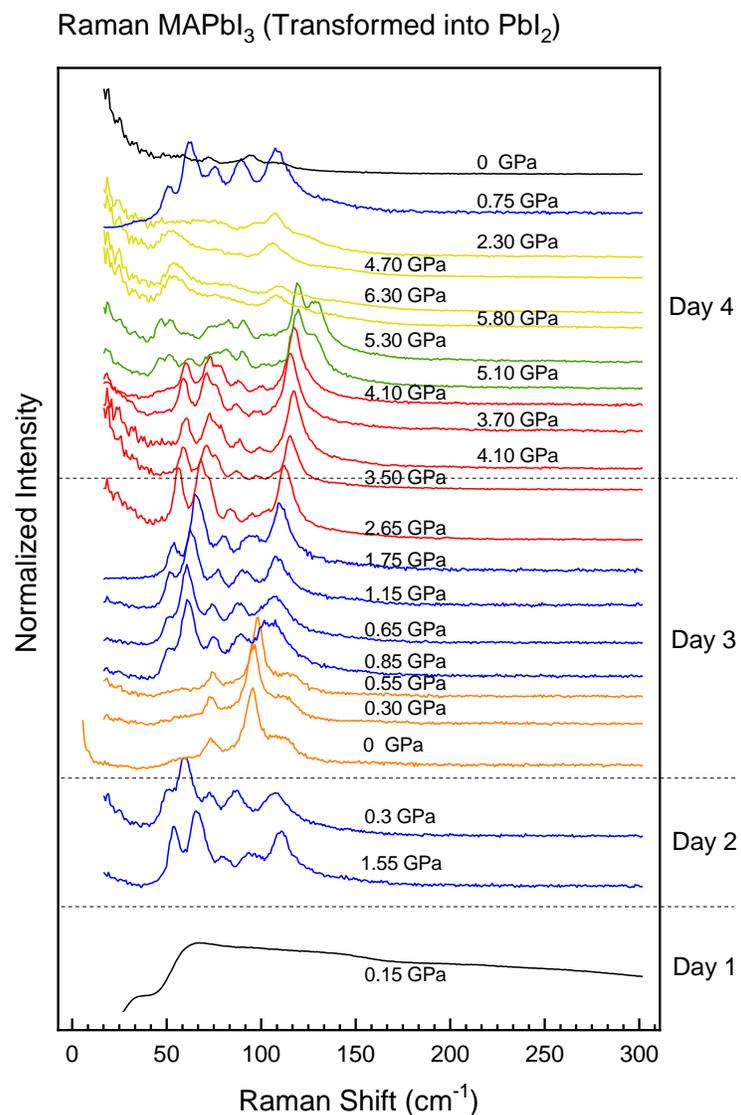


Figure S 3: Raman spectra obtained when applying pressure on a MAPbI₃ sample using a different pressure medium (4:1 methanol-ethanol mixture possibly with traces of water) rather than propanol. After an initial cycle of pressurization, the Raman spectra of the sample coincide with those obtained by for PbI₂. The horizontal dotted lines mark the different days at which the measurements were performed.

A comparative of the effects of pressure on MAPbI₃ and PbI₂

Here we report on an accidental finding with implications for the understanding of the high-pressure structural behavior of MAPbI₃. In another experiment, we loaded the DAC using the usual 4:1 methanol/ethanol mixture. Most likely due to the presence of traces of water in the mixture, MAPbI₃ unequivocally transformed into PbI₂ under compression at a moderate pressure of about 1 GPa. The evidence of this transformation is seen in Figs. S3 and S4. In the former, we display all the Raman spectra as taken chronologically during this separate experiment, whereas in the latter we compare side-by-side the Raman results obtained for 2H-PbI₂ under pressure⁶ with spectra measured in the present experiment at similar pressures. The direct comparison clearly indicates, for example, that on day 2, MAPbI₃ had already transformed into PbI₂, for the similitude of the Raman spectra is just striking. We point out that the PL signal is completely lost once the sample underwent the pressure-induced transition from MAPbI₃ to PbI₂, i.e., we are not able to record any spectrum similar to the ones reported by Saitoh et al. for PbI₂ single crystals measured under pressure but at low temperature.⁷ Moreover, during the second upstroke and at around 0.6 GPa, the phase transition from the 2D (layered) form of 2H-PbI₂ into a 3D crystal structure is observed in Raman scattering, exactly as reported.⁶ This phase transition was also observed at the same pressure but a much lower temperature of 77 K.⁷ Jayaraman et al.⁶ further reported two subsequent phase transitions of 2H-PbI₂, one at 3 GPa to a phase with a less symmetric structure and another at around 4 GPa to an amorphous phase. Above 5.5 GPa, in contrast, we find an additional phase transformation of PbI₂, not previously reported. In our case, we emphasize that the structural changes were only partially reversible upon depressurization. As indicated by the Raman spectrum taken by decreasing pressure to 0.75 GPa of Fig. S3, the sample recovered the signature of the 3D crystalline phase of PbI₂. Nevertheless, when the DAC was finally opened, the sample decomposed completely and became a dark reddish paste, exhibiting the featureless Raman

spectrum of Fig. S3 (0 GPa spectrum at the top). The strong PL of MAPbI₃ also disappeared as soon as the Raman spectra corresponded to the ones of lead iodide.

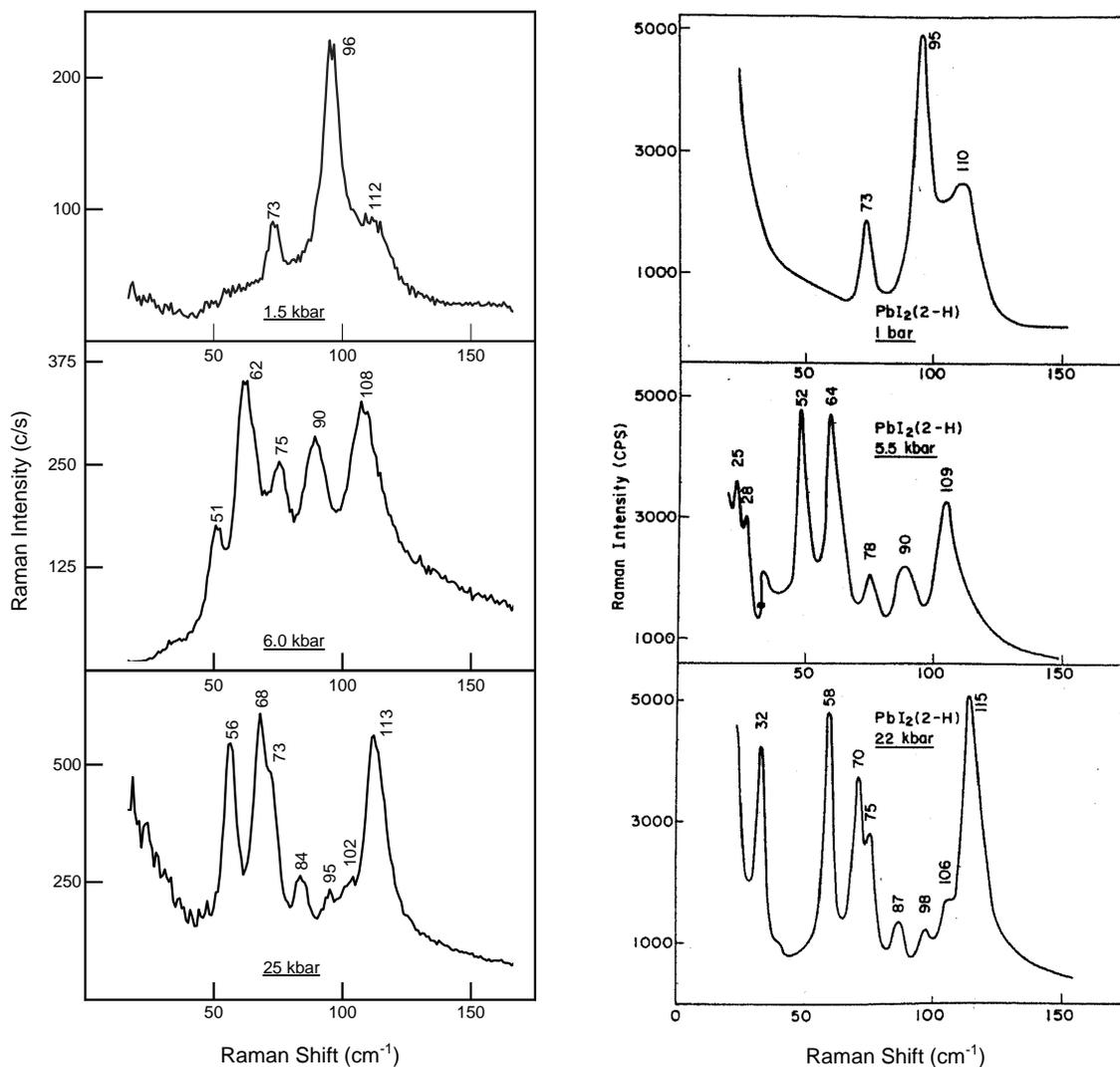


Figure S 4: The panels on the right hand side correspond to a reproduction of Fig. 1 of the work by Jayaraman et al.,⁶ which shows Raman spectra of 2H-PbI₂ measured at the pressures where three different phases were stable. The panels on the left hand side display Raman spectra of the MAPbI₃ sample after its presumable transformation into lead iodide measured at similar pressures as by Jayaraman et al.⁶ The similitude of the spectra, regarding lineshape as well as the position of the Raman peaks, is so high that there is no doubt that the full pressure-induced transformation of MAPbI₃ into PbI₂ has taken place.

As mentioned in the manuscript, the Raman spectra of PbI_2 at pressures above 5.5 GPa, as determined in the present experiment, and those of MAPbI_3 in the phases where the MA molecules are locked in the cage voids are astonishingly similar (see also Fig. 6 of the manuscript). We are thus lead to the conclusion that both materials share similar structural units in these high pressure phases. Hybrid organic-metal-halide perovskites are described by the general formula $(\text{R-NH}_3)_n\text{MX}_m$, where R is an organic group, X is a halogen atom (X=I, Br, Cl), and M is a metal (M=Pb, Sn, Ge). The pair of indices (n, m) control the stoichiometry and charge neutrality of the compound. They also determine crystal packing and dimensionality of the structure, ranging from three-dimensional (3D) corner-shared perovskite structures for $(n, m)=(1, 3)$, 2D layered perovskites for $(n, m)=(2, 4)$ to 0D structures with isolated inorganic octahedra. In this sense, 2H- PbI_2 , a 2D layered semiconductor, can be thought as pertaining to this family of compounds having indices $(n, m)=(0, 2)$. In addition, the application of high hydrostatic pressure usually leads to structural phase transformations, where phases exhibiting a higher metal-halogen atom coordination are increasingly favored for higher compression. Hence, it is likely that certain correlation exists between the pressure-induced structural changes of different members of the compound family.

On the one hand, the fact that the structural changes in MAPbI_3 are fully reversible is evidence that the sixfold coordination of the Pb atoms to the iodides is preserved under pressure and that the high pressure phases differ from each other only in the degree of tilting and deformation of the corner-shared PbI_6 octahedra (see sketch in Fig. S5). Furthermore, due to the observed locking of the MA molecules in the voids, the phase setting in above 2.7 GPa is likely to be orthorhombic. On the other hand, recent simulations performed through searching algorithms like the swarm-intelligence CALYPSO method⁸ predict for 2H- PbI_2 a series of phase transformations from the layered $P\bar{3}m1$ structure to an orthorhombic $Pnma$ and a tetragonal $I4/mmm$ one at 2.5 and 27 GPa, respectively. Precisely the tetragonal phase, which is characterized by a tenfold coordination

of PbI_{10} dodecahedral units, is a good candidate for the high-pressure phase we found above 5.5 GPa in PbI_2 , in spite of the large discrepancy in the calculated and measured transition pressures. The similar shape of the Raman spectra of both materials displayed in Fig. S3 and Fig. 6 of the manuscript might be due to the similarity of the structural building blocks, as depicted in Fig. S5. Another interesting observation is that the Raman mode frequencies of PbI_2 are redshifted compared to those of MAPbI_3 even though the Raman spectra of the latter were measured at lower pressures (see Fig. 6 of the manuscript). We believe that this is a consequence of the lengthening of the Pb-I bonds imposed by a higher coordination of the structure having dodecahedral structural units rather than octahedral ones.

In summary, the main conclusion from the results of this section is that the high-pressure phase

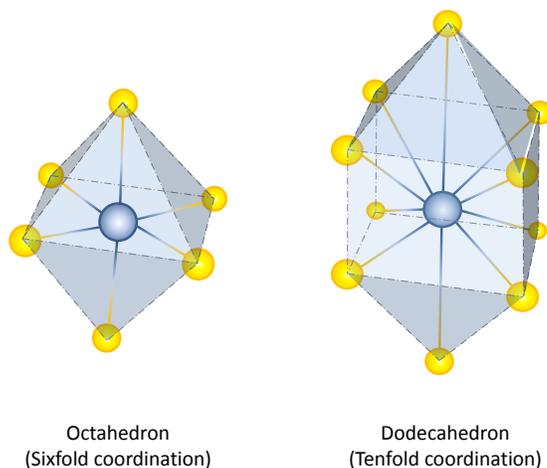


Figure S 5: Sketch of the structural units corresponding to PbI_6 octahedra and PbI_{10} dodecahedra from which the crystalline structure of the high pressure phases of MAPbI_3 and PbI_2 might be constructed. The grey central atom is Pb and the yellow balls represent the I atoms. The pb-I bonds are necessarily longer in the dodecahedron due to the higher coordination.

of MAPbI₃ above 3.3 GPa and the one of PbI₂ above 5.5 GPa, reported here for the first time, do share similar structural units, making the Raman spectra to look alike. Though, by no means can be inferred that MAPbI₃ has transformed into PbI₂ at those high pressures. In spite of the (accidental) similarity of the PL emission from PbI₂ at around 2 GPa⁷ and that of MAPbI₃ in the fourth high pressure phase, there are unambiguous facts that rule out such a transformation. The strongest one is the full reversibility of the pressure-induced changes in the vibrational as well as optical properties of MAPbI₃ as compared to the complete irreversibility of its humidity-related degradation into PbI₂.⁹

References

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