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Alla Arakcheeva,<sup>a</sup>\* Volodymyr Svitlyk,<sup>b</sup> Eleonora Polini,<sup>c</sup> Laura Henry,<sup>b</sup> Dmitry Chernyshov,<sup>d</sup> Andrzej Sienkiewicz,<sup>a,e</sup> Gaétan Giriat,<sup>a</sup> Anastasiia Glushkova,<sup>a</sup> Marton Kollar,<sup>a</sup> Bálint Náfrádi,<sup>a</sup> Laszlo Forro<sup>a</sup> and Endre Horváth<sup>a</sup>

<sup>a</sup>Ecole Polytechnique Fédérale de Lausanne, School of Basic Sciences, Institute of Physics, Laboratory of Physics of Complex Matter (SB IPHYS LPMC), PH D2 445 (Bâtiment PH), Station 3, Lausanne, CH-1015, Switzerland, <sup>b</sup>ID27 High Pressure Beamline, ESRF, 71 Avenue des Martyrs, Cedex 9, Grenoble, 38043, France, <sup>c</sup>Department of Physics, Università di Roma La Sapienza, Piazzale Aldo Moro, 5, Roma RM, 00185 Italy, <sup>d</sup>SNBL, ESRF, 71 Avenue des Martyrs, Cedex 9, Grenoble, 38043, France, and <sup>e</sup>ADSresonances SARL, Route de Genève 60B, Préverenges, CH-1028, Switzerland. \*Correspondence e-mail: alla.arakcheeva@epfl.ch

The photovoltaic perovskite, methylammonium lead triiodide [CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (MAPbI<sub>3</sub>)], is one of the most efficient materials for solar energy conversion. Various kinds of chemical and physical modifications have been applied to MAPbI<sub>3</sub> towards better understanding of the relation between composition, structure, electronic properties and energy conversion efficiency of this material. Pressure is a particularly useful tool, as it can substantially reduce the interatomic spacing in this relatively soft material and cause significant modifications to the electronic structure. Application of high pressure induces changes in the crystal symmetry up to a threshold level above which it leads to amorphization. Here, a detailed structural study of MAPbI<sub>3</sub> at high hydrostatic pressures using Ne and Ar as pressure transmitting media is reported. Singlecrystal X-ray diffraction experiments with synchrotron radiation at room temperature in the 0–20 GPa pressure range show that atoms of both gaseous media, Ne and Ar, are gradually incorporated into MAPbI<sub>3</sub>, thus leading to marked structural changes of the material. Specifically, Ne stabilizes the highpressure phase of Ne<sub>x</sub>MAPbI<sub>3</sub> and prevents amorphization up to 20 GPa. After releasing the pressure, the crystal has the composition of  $Ne_{0.97}MAPbI_3$ , which remains stable under ambient conditions. In contrast, above 2.4 GPa, Ar accelerates an irreversible amorphization. The distinct impacts of Ne and Ar are attributed to differences in their chemical reactivity under pressure inside the restricted space between the PbI<sub>6</sub> octahedra.

#### 1. Introduction

MAPbI<sub>3</sub> is currently considered as one of the most promising compounds in photovoltaic technologies for making cheap and highly efficient solar cells (Green *et al.*, 2014; Weber *et al.*, 2015). One of the hurdles which reduces the enthusiasm for practical applications of MAPbI<sub>3</sub> is its content of lead which confers toxicity on this material (Benmessaoud *et al.*, 2016). Therefore, it would be highly desirable to replace lead with a non-toxic element, while still preserving the high light conversion efficiency. The *conditio sine qua non* for achieving this goal is a better understanding of the microscopic origin of this high energy conversion efficiency. There are opinions that the rotation or other type of motion of methylammonium cations (MA) introduces a slightly indirect band gap in this material, which extends the lifetime of photoelectrons (Motta *et al.*, 2015), helping them to flow out of the material as a

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current. Valuable information about the role of the cation can be obtained by studying its behaviour in the lattice under high pressure (Ou et al., 2016). The perovskite crystal structure of MAPbI<sub>3</sub> is very flexible due to a large interstitial space (of  $\sim$ 8 Å in diameter), where the small ( $\sim$ 1.5 Å) linear cation is located. The PbI<sub>6</sub> octahedra and the cations interact via weak hydrogen bonds. The strength and the conformation of the hydrogen bonds can be influenced either by the presence of captured exogenous substances, such as water (Arakcheeva et al., 2016), or by external factors such as pressure or temperature, leading to changes in the symmetry of the unit cell. A recently published extended review (Lü et al., 2017) on the pressure-induced evolution of the structure and the physical properties of organic-inorganic halide perovskites demonstrates a poor reproducibility of the changes. This calls for more investigations to uncover the underlying mechanisms. Fig. 1 shows a schematic representation of the two major pressure-induced structural transformations in MAPbI<sub>3</sub>, a phase transition and amorphization, reported in the literature together with the ones obtained in the present study. At very low pressures (0.1-0.3 GPa), a first-order phase transition from the tetragonal body-centred to the body-centred (pseudo) cubic unit cell takes place (Fig. 1, blue to red lines). The amorphization of the compound occurs after the structural phase transition (Fig. 1, black line). However, in different experiments the onset of the amorphization has been observed under different pressures, and the pressure transmitting medium (PTM) could be considered as a factor affecting the pressure-induced transformation of MAPbI<sub>3</sub> (Fig. 1). Such an effect has already been observed in organic





Schematic overview of the pressure-induced transformation of MAPbI<sub>3</sub> at room temperature. Top panel: influence of the PTM on the transformation. The thickness of the red and black lines represents schematically the relative content of the (pseudo) cubic and amorphous phases shown, respectively, in the bottom panel. Bottom panel: relations between the unit cells of different phases. Unit-cell parameters:  $a_{\rm pr} \simeq 6.4$  Å for the primitive perovskite cubic cell (green line);  $a = b \simeq a_{\rm pr} \sqrt{2} \simeq 8.8$  Å and  $c \simeq 2a_{\rm pr} \simeq 12.7$  Å for the tetragonal body-centred cell (blue) under ambient condition;  $a \simeq b \simeq c \simeq 2a_{\rm pr} \simeq 12.3$  Å for the body-centred (pseudo)cubic cell (red) under high pressure. The data are taken from: Capitani *et al.* (2016) for no PTM (None); Jiang *et al.* (2016) for silicon oil (Sioil); Wang *et al.* (2015) for non-specified PTM (Unknown); Szafrański & Katrusiak (2016) for propanol. Data corresponding to Ar and Ne (yellow background) are from the present work.

compounds (Zakharov *et al.*, 2016) and also in some minerals (Ardit *et al.*, 2014; Sato *et al.*, 2013; Guńka *et al.*, 2015; Lobban *et al.*, 2002). This provided the motivation for the present work on studying the influence of PTM on the structure of MAPbI<sub>3</sub>. We have chosen two noble gaseous media, Ne and Ar, which are among the most hydrostatic PTMs and have distinct atomic radii: Ne (0.38 Å) and Ar (0.71 Å). Single-crystal synchrotron X-ray diffraction (XRD) measurements provided a precise data set, which allowed structure determination as a function of pressure with the best precision. Surprisingly, we found that under high pressure both Ar and Ne were incorporated into the structure. Moreover, the pressure-induced phase of Ne<sub>0.97</sub>MAPbI<sub>3</sub> remained stable and highly crystalline after decompression.

#### 2. Experimental

#### 2.1. Synthesis and crystallization

The preparation of MAPbI<sub>3</sub> single crystals has been reported elsewhere (Arakcheeva *et al.*, 2016). Several crystals were initially tested for their crystal structure and crystal quality at ambient conditions. All of them showed the space group *I*422 crystal symmetry with the unit-cell parameters and the atomic coordinates identical to those reported by Arakcheeva *et al.* (2016). Preliminary diffraction measurements under high pressure showed as expected that the starting quality of the crystal (degree of mosaic and strains) has a significant effect on the high-pressure transformation (Fig. S1). Therefore, only the highest quality crystals have been selected for the final diffraction experiments.

#### 2.2. Single-crystal synchrotron XRD experiments

Room-temperature (293 K) high-pressure (up to 20.27 GPa) XRD data were collected at the ID27 High Pressure Beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble. Diamond anvil cells were used with rhenium gaskets and Ne or Ar gases as the PTM to generate hydrostatic conditions. The X-ray wavelength was set to 0.3738 Å. The minimal linear size of the crystals was about 10 µm. Diffraction data were recorded with a Mar165 CCD detector and the pressure was measured using the ruby fluorescence technique (Syassen, 2008). After decompression, additional measurements were conducted on the Necontaining crystal to determine its structure under ambient conditions. CrysAlis PRO (Rigaku Oxford Diffraction, 2014) and JANA2006 (Petříček et al., 2014) software packages were used for data processing and structural refinement, respectively. Experimental details are listed in Tables S1 and S2 and are illustrated in Fig. 2 and also in Figs. S1, S2 and S3.

**2.2.1. Structure determination**. The general scheme of the structure determination is illustrated in Fig. 3 using the example of the crystal at ambient conditions and under 0.69 GPa up to 20.27 GPa pressures with Ne as the PTM. The starting (pristine) and the released (after exposure to the highest pressure) crystals are shown next to each other for comparison. The most probable symmetry of the structure at

each pressure was determined by testing the inorganic framework for all possible space groups in all possible crystallographic systems (cubic, tetragonal, trigonal and orthorhombic). Next, after the refinement of the atomic positions of Pb and I [Fig. 3(a)], difference electron density maps were calculated for each case [Fig. 3(b)]. The pristine crystal can be characterized by the maxima in the expected MA positions [dark-blue circles in Fig. 3(b)]. These maxima are also perfectly identified at 0.69 GPa and for the released crystal, whereas they are absent at 20.27 GPa. However, even stronger and more localized maxima [cyan circles in Fig. 3(b)] are clearly visible for each pressure, with the exception of the starting (pristine) case. These additional maxima are attributed to Ne atoms, giving a compatible electron density contribution [Fig. 3(c)]. At 20.27 GPa, the usual MA positions show nearly zero electron density and only the Ne-attributed maxima are observable. We have to emphasize that these maxima could not be fitted with displaced MA cations. The schematic diagrams of the crystal structure for each pressure after including MA and/or Ne in the refined models are shown in Fig. 3(c). The residual electron density maps calculated after the refinements have values close to zero [Fig. 3(d)], this supports the models.

Refinement of all atomic parameters for MA and Ne helped to confirm or correct the space group selected previously for the framework at each pressure. A similar procedure for the structure determination was used for all applied pressures for both Ne and Ar as the PTM.

As expected, the inclusion of Ne and Ar in the structure has a varying effect on the symmetry and the bulk modulus at different pressures. The resulting structures made it possible to determine the interatomic distances, and consequently the nature and hierarchy of interactions between various components of each structure.

The basic crystallographic information for eight different pressures with Ne as the PTM and six different pressures with Ar as the PTM is provided in Tables 1 and 2, respectively, and is visualized in Fig. 4. Further details are listed in Tables S1 and S2. It should be noted that, despite the reflections-to-parameters ratio which is 5.6 and 4.1 for the Ne-containing crystal at 16.43 and 20.27 GPa, respectively, the criteria R, wR, S = 0.051, 0.057, 1.44 for 16.43 GPa and 0.043, 0.064, 1.49 for 20.27 GPa, and the residual electron density  $\rho_{max}$ ,  $\rho_{min} = 0.58$ ,  $-0.60 \text{ e } \text{Å}^{-3}$  for 16.43 GPa and 1.06,  $-1.25 \text{ e } \text{Å}^{-3}$  for 20.27 GPa (column VI and VII in Table S1) show that the corresponding structure solutions are correct. These structures



#### Figure 2

The XRD patterns illustrating the pressure-induced transformation of MAPbI<sub>3</sub> with (a) Ne and (b) Ar as PTM. The powder XRD patterns calculated from the single-crystal experiments are presented at the logarithmic scale. Sections of the reciprocal space are shown for l = 0. The axes h, k (H, K) specific only for the tetragonal (pseudo-cubic) modification are emphasized in blue (red).

obtained at the highest pressures are essential for understanding the Ne intercalation, which is also confirmed by the presence of Ne in the released crystal under ambient conditions.

#### 3. Results and discussion

#### 3.1. The high-pressure NeMAPbI<sub>3</sub> compounds

The crystal structure at room temperature (293 K) was determined for 0.69, 1.5, 2.69, 4.56, 7.4, 16.43 and 20.27 GPa pressures and for ambient pressure after decompression (Table 1). Above 4 GPa an amorphous phase appears, coexisting with the crystalline one. The amorphous contribution slowly grows upon further increase of pressure and completely disappears after pressure is released (Fig. S1).

The XRD data obtained at 0.11 GPa indicate the coexistence of two phases: a tetragonal phase, characteristic of ambient pressure, and a pseudo-cubic phase, which is typical for higher pressures (Fig. S3). This is consistent with the firstorder phase transition, which was reported before between 0.3 GPa and 0.4 GPa (Capitani et al., 2016; Szafrański & Katrusiak, 2016; Francisco-López et al., 2018). However, for the pseudo-cubic phase, we found the space group  $R\bar{3}$ , which differs from the cubic  $Im\bar{3}$  and orthorhombic  $Imm^2$  reported previously by Szafrański & Katrusiak (2016) and Capitani et al. (2016), respectively. We observed a second phase transformation between 2.69 GPa and 4.56 GPa. It is also in good agreement with the literature value of 2.5 GPa (Szafrański & Katrusiak, 2016) and 2.7 GPa (Francisco-López et al., 2018). Even so, in contrast to the reported space group  $Im\bar{3}$ (Szafrański & Katrusiak, 2016), only its orthorhombic subgroup, Im2m, was found to describe the symmetry of the phase above 4.56 GPa. Furthermore, for the first time we observed a third transformation, from the orthorhombic to a tetragonal phase (space group I4/mmm) between 7.4 GPa and



#### Figure 3

Determination of the MA and Ne positions in the crystal structure of MAPbI<sub>3</sub> at selected pressures. Projections of the relevant fragments of the structure onto the *ac* plane are in (*a*) and (*c*). Small dots indicate I atoms in the plane for which the difference electron density maps are shown in (*b*) and (*d*) with positive (red) and negative (blue) areas. (*b*) The maps were calculated using only Pb and I atoms. The maxima of the difference electron densities are identified with MA cations (dark-blue circles) and Ne atoms (cyan circles). The density varies: from -0.32 to 1.58 e Å<sup>-3</sup> for the released crystal at *P* = 1 atm; from 0.20 to 0.41 e Å<sup>-3</sup> for the pristine crystal at *P* = 1 atm; from -1.44 to 1.97 e Å<sup>-3</sup> for *P* = 0.69 GPa; from -1.13 to 1.86 e Å<sup>-3</sup> for *P* = 20.27 GPa. (*d*) The residual electron density maps were calculated using all atoms of the structure. The residual electron density varies: from -0.31 to 0.51 e Å<sup>-3</sup> for *P* = 1; from -0.27 to 0.23 e Å<sup>-3</sup> for the pristine crystal at *P* = 1 atm; from -1.06 to 1.07 e Å<sup>-3</sup> for *P* = 0.69 GPa; from -1.06 to 1.07 e Å<sup>-3</sup> for *P* = 0.69 GPa; from -0.54 to 0.56 e Å<sup>-3</sup> for *P* = 20.27 GPa.

Table 1	
Crystallographic data and composition for Ne-MAPbI <sub>3</sub> in the 0–20 GPa pressure range.	

	Ne <sub>x</sub> MAPbI <sub>3</sub>	Ne <sub>x</sub> MAPbI <sub>3</sub>	Ne <sub>x</sub> MAPbI <sub>3</sub>	Ne <sub>0.97</sub> MAPbI <sub>3</sub>
P (GPa)	$0.69 \rightarrow 1.5 \rightarrow 2.69$	$4.56 \rightarrow 7.4$	$16.43 \rightarrow 20.27$	1 atm (released)
Crystal system	Trigonal	Orthorhombic	Tetragonal	Tetragonal
Space group	RĪ	Im2m	I4/mmm	I422
a (Å)	$17.3128(9) \rightarrow 17.0325(9) \rightarrow 16.7757(9)$	$11.435(3) \rightarrow 11.196(3)$	$10.700(5) \rightarrow 10.538(5)$	8.876(1)
b (Å)	= <i>a</i>	$11.437(3) \rightarrow 11.197(3)$	= <i>a</i>	= <i>a</i>
c (Å)	$10.6019(5) \rightarrow 10.4338(5) \rightarrow 10.2267(5)$	$11.442(3) \rightarrow 11.201(3)$	$10.620(10) \rightarrow 10.3793(11)$	12.672(1)
x in $Ne_x$	$0.42(1) \rightarrow 0.60(1) \rightarrow 0.91(1)$	$1.10(1) \rightarrow 1.41(1)$	$2.17(1) \rightarrow 2.50(1)$	0.97

Table 2

Crystallographic data and composition for Ar-containing MAPbI<sub>3</sub> in the 0–2.4 GPa pressure range.

	Ar <sub>x</sub> MAPbI <sub>3</sub>	Ar <sub>x</sub> MAPbI <sub>3</sub>
P (GPa)	$0.18 \rightarrow 0.49 \rightarrow 0.98$	$1.34 \rightarrow 2.10 \rightarrow 2.39$
Crystal system	Tetragonal	Orthorhombic
Space group	$P4_2bc$	Immm
a (Å)	$8.850(5) \rightarrow 8.7468(15) \rightarrow 8.7222(15)$	$12.1294(12) \rightarrow 12.0192(10) \rightarrow 11.900(11)$
$b(\mathbf{A})$	= a	$12.1415(12) \rightarrow 12.0195(10) \rightarrow 11.990(1)$
c (Å)	$12.520(5) \rightarrow 12.398(10) \rightarrow 11.9979(15)$	$12.1734(15) \rightarrow 12.0213(10) \rightarrow 11.920(1)$
x in Ar <sub>x</sub>	$0.76(1) \rightarrow 1.00(1) \rightarrow 1.34(1)$	$1.40(1) \rightarrow 1.78(1) \rightarrow 1.75(1)$

16.43 GPa. The unit cells and space groups corresponding to each phase are shown in Fig. 4(a)(i). We explain the difference in the symmetry, the presence of a third phase transition and



#### Figure 4

Evolution of crystallographic characteristics of MAPbI<sub>3</sub> under pressure with (*a*) Ne and (*b*) Ar as the pressure transmitting media (PTM). Panels a(i) and b(i) show the symmetry transformation of the unit cell. Unit cells are shown in different colours for different crystallographic systems in relation to a primitive perovskite cube (green line). Panels a(ii), b(ii)show the pressure dependence of the unit-cell volume and crystal density. Points in the diagrams are coloured according to the unit cells in panels (i). Green and black points correspond to the pristine and released crystals, respectively.

the lack of amorphization up to 20 GPa by the intercalation of Ne, which we found for the high-pressure phases.

Fig. 5 illustrates the evolution of the NeMAPbI $_3$  structure under compression.

First, we observe evolution of the compound composition [Fig. 5(b)]: (i) a gradual pressure-induced growth in the Ne content and (ii) a gradual disappearance of the MA cation from the detectable, *i.e.* periodic over a long range, positions.

The observation (i) concerns positions of Ne atoms and their corresponding site occupancies. The intercalated Ne atoms are located in large voids of the inorganic framework, more precisely at the faces of the primitive perovskite cube [Fig. 5(a)], with a gradual increase in the occupancy of these sites upon compression [Fig. 5(d) and Figs. S4a and S5 in the supporting information]. The four neighbouring I atoms surround each Ne atom. The average occupancy of Ne sites starts at approximately one-third in the low-pressure phases and goes up with pressure, eventually approaching one when Ne atoms sit at each face. At 20.27 GPa, Ne sites are fully occupied for the faces of only four out of six possible orientations, and the remaining two are half occupied. One can therefore expect that even higher pressure is required in order to achieve the full occupancy. The corresponding composition, Ne<sub>3</sub>PbI<sub>3</sub>(MA), reflects the maximum possible Ne content in the structure.

The observation (ii) needs some extended explanation. A reversible transformation, which restores all the long-rangeordered positions of MA in the released crystal at ambient pressure (Fig. 3), indicates that this cation can be in two different states in the high-pressure crystal: the long-rangeordered state (*i.e.* periodic) and the randomly distributed one (*i.e.* non-periodic). In order to emphasize these two states of MA, we use the Ne<sub>x</sub>MA<sub>y</sub>PbI<sub>3</sub>(MA)<sub>1-y</sub> designation for the chemical formula, where indices y and (1 - y) denote the relative quantities of the long-range-ordered and the randomly distributed MA, respectively. The presence of two

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states for the MA cation is a direct confirmation of the assumption that the long-range ordering of MA is violated under high pressure, proposed by Ou *et al.* (2016), Capitani *et al.* (2016) and Szafrański & Katrusiak (2016). According to this assumption, a lack of long-range ordering of MA leads to

destruction of the inorganic (Pb,I)-framework, which is kept by the I–MA periodic interactions. Indeed, a decrease in the amount for long-range-ordered MA leads to a huge increase in the atomic displacement parameters for I atoms (Fig. 6), which is a sign of the destruction of the inorganic framework.



Figure 5

Schematic diagram of the NeMAPbI<sub>3</sub> structure evolution under compression and after pressure release. Panel (*a*) indicates the arrangement of Ne atoms at the faces of the primitive perovskite cubic unit cell. These faces are represented by cyan squares formed by I atoms. Depending on pressure, some of the Ne sites can be empty or partially occupied. Panel (*b*) shows a pressure-induced change of the crystal composition. In the chemical formula, *y* and (1 - y) refer to MA at the long-range-ordered and the non-localized (non-periodic) positions, respectively. Panel (*c*) presents the shortest interatomic distances for Ne–I, Ne–MA and I–MA under different pressures. Panel (*d*) demonstrates the main trend of the pressure-induced structure evolution, that is of a gradual increase in the number and occupancy of Ne sites, indicated in (*a*). Unexpectedly, all these sites are also partially occupied in the released crystal.



Figure 6

Pressure-dependent atomic displacement parameters (ADP) of I atoms for the representative fragment of the inorganic framework. Panel (a) shows the fragment under three pressures with the long-range-ordered MA cation. Panel (b) shows the fragment under two pressures with the partially long-range ordered MA cation. Panel (c) presents the fragment corresponding to the absence of the long-range-ordered MA cation. The ADP ellipsoids are shown with 50% probability for each pressure.

Destruction of the inorganic framework leads to compound amorphization. However, we observed that with the Ne PTM. the periodic crystal structure still exists up to 20 GPa. The reasons of this can be understood from the analysis of the Ne-I, Ne-AM and I-MA interatomic distances found for the longrange-ordered MA cation [Fig. 5(c)]. The short distances MA-Ne of  $\sim$ 1.9 Å indicating the corresponding interaction at P < 3 GPa can be recognized as unstable with respect to pressure, since the content of the long-range-ordered MA rapidly reduces from 0.5 (4.56 GPa) to 0.25 (7.4 GPa) per chemical formula, and the long-range-ordered MA is no longer observed for  $P \ge 16.3$  GPa. If the expected rapid amorphization does not appear, it means that stabilization of the (Pb,I)-framework is kept by another stabilizer, which is different from MA; it is Ne atoms in the considered case. Indeed, for P > 4 GPa, the loss of the long-range order for more than 50% of MA switches the shortest interatomic distance (i.e. the strongest interaction of Ne) from Ne-MA to Ne-I [Fig. 5(c)]. Consequently, the Ne-I interactions can be considered as the cause of stabilization of the framework, preventing the amorphization.

The stabilizing role of Ne under high pressure is also confirmed by the distortions observed in the (Pb,I)-framework: the minimal distortions (the I-Pb-I angle  $\simeq 88.4$ -90.3° instead of the ideal 90° and the Pb-I-Pb angle  $\simeq 178$ -180° instead of the ideal 180°) were found in tetragonal structures at the highest pressure, when the long-range order MA is lost and the content of Ne is maximal (Table S3).

Thus, the progressive intercalation of Ne is the general trend in the pressure evolution of the NeMAPbI<sub>3</sub>. The phenomenon is driven by the Ne-I interaction, which is substantially enhanced above 4 GPa.

Surprisingly, the occupation of Ne sites in all directions is preserved in the released structure under ambient pressure, but with a much smaller probability of approximately onethird [Fig. 5(*d*)]. The mean Ne–MA and Ne–I distances in the released structure, 2.83 Å and 2.78 Å, respectively, are very similar [Fig. 5(*c*)]. The minimum Ne–MA distance of approximately 2.3 Å in the released crystal can be responsible for this stabilization. However, this is the distance between the partially occupied Ne and MA sites, so it is problematic to say with certainty whether such separation is indeed realized.



#### Figure 7

Sketch of the ArMAPbI<sub>3</sub> structure evolution under compression. Panel (*a*) schematically shows a plane (pinkish grey square) where the Ar atoms are located. The plane is defined by I atoms and the centre of the MA cation. Panel (*b*) shows the pressure-induced change of the crystal composition. Panel (*c*) presents the shortest interatomic distances for Ar–I, Ar–MA and I–MA under different pressures. Panel (*d*) demonstrates the main trend of the pressure-induced structure evolution: below 1 GPa, Ar, MA and I atoms are arranged in chains, along the shortest Ar–I and Ar–MA distances, shown in (*c*); under increasing pressure, the number of the Ar positions rises, and the crossing chains form a layer. Each pinkish grey rectangle corresponds to the one shown in (*a*). Pinkish grey-coloured segments indicate the occupancies of the Ar sites.

In the 0–20 GPa pressure range the bulk modulus  $B_0$ , calculated using the Birch–Murnaghan model (Birch, 1947), varies from 5.3 GPa at the lowest to 10.6 GPa at the highest pressure. These numbers fall within the spread of values in the literature (Capitani *et al.*, 2016; Jaffe *et al.*, 2016) even for the crystalline phase at 20 GPa, which was absent for other PTMs.

#### 3.2. The high-pressure ArMAPbI<sub>3</sub> compounds

The structure was determined at pressures of 0.18, 0.49, 0.98, 1.34, 2.1, and 2.39 GPa at room temperature (Table 2). Above 1.34 GPa an amorphous phase appears, coexisting with the crystalline one. The amorphous contribution grows rapidly with increasing pressure until no crystalline phase can be observed above 3.6 GPa (Fig. S2). This amorphization is irreversible in our experiments.

The tetragonal unit-cell parameters, characteristic for the ambient conditions, have been identified in the ArMAPbI<sub>3</sub> structure up to 1 GPa [Table 2 and Fig. 4(b)(i)]. The space group  $P4_{2}bc$ , which is new for the title compound, turned out to be the best fit in the 0.18-0.98 GPa pressure range. Only one transformation of this unit cell was detected for ArMAPbI<sub>3</sub>, happening between 1 GPa and 1.3 GPa. The pseudo-cubic orthorhombic unit cell [Fig. 4(b)(i)] and the *Immm* space group are characteristic for the lattice for P >1 GPa (Table 2). No distortion in the long-range order was detected for the MA cation. In comparison to NeMAPbI<sub>3</sub>, growth in the Ar content as a function of pressure is 5.5 times larger, reaching the composition Ar<sub>14</sub>MAPbI<sub>3</sub> at 1.34 GPa. In the case of Ne PTM, the nearly equivalent composition, Ne<sub>1.41</sub>MA<sub>0.25</sub>PbI<sub>3</sub>(MA)<sub>0.75</sub>, occurs at 7.4 GPa (Tables 1 and 2). This indicates a much stronger interaction of MAPbI<sub>3</sub> with Ar than with Ne.

The pressure-induced structural evolution of  $ArMAPbI_3$  (Fig. 7) is associated with a gradual growth in the Ar content

[Fig. 7(*b*)], accompanied by the contraction of the Ar–I and Ar–MA distances [Fig. 7(*c*)]. For P < 1 GPa, the MA cations, Ar and I atoms closest to each other are arranged into chains, which polymerize in two dimensions upon further compression [Fig. 7(*d*)]. Influence of the lattice contraction on the chain geometry is illustrated in Fig. 8.

The shortest interatomic distances of  $\sim 2$  Å found for Ar–I and Ar–N (MA) at 2.1 and 2.39 GPa can be considered as a reasonable approximation if two arguments are taken into account. First, the value of 1.84 Å was theoretically predicted for the Ar–N separation for ambient pressure (Novak & Fortenberry, 2016). Second, large and prolate ADP ellipsoids of the I atoms imply an anharmonic character of the atomic displacements, which indicates that the actual Ar–I distances are longer.

Nevertheless, we consider the dramatic reduction of the minimum Ar–MA and Ar–I distances at  $P \ge 2$  GPa [circled by red line in Fig. 7(c)] as a trigger for the complete and irreversible structure amorphization. In fact, we recorded a crystalline state at the time of its destruction.

Thus, the pressure-induced formation of the stable I–Ar– MA–Ar– chains and their polymerization [Fig. 7(d)] is at the origin of the structural evolution and amorphization of ArMAPbI<sub>3</sub>.

Detailed characteristics of the progressive changes in the  $ArMAPbI_3$  structure under pressure are also given in the supporting information (Figs. S4b, S6 and S7).

3.3. Different impact of Ne and Ar as a pressure transmitting medium

The present results show that both Ne and Ar interact with MAPbI<sub>3</sub>, but in different ways. Interactions between Ne and I atoms stabilize the inorganic (Pb,I)-framework up to 20 GPa and suppress amorphization of the crystal, despite the



#### Figure 8

Pressure-induced transformation of the tetragonal ArMAPbI<sub>3</sub> phase. (a) Position of the I–Ar–MA–Ar– group within the (Pb,I)-framework. (b) Deformation of the group configuration and its connection to I atoms. Pink-coloured segments indicate the occupancies of the Ar sites. The MA–Ar and Ar–I interatomic distances are given in Å.

vanishing of the long-range ordering of MA. Ne serves as a structural stabilizer instead of MA for pressures higher than 4 GPa. Unlike Ne, Ar interacts with both I and MA even under low pressure of 0.18 GPa. These interactions accelerate the irreversible amorphization, which starts at P > 2 GPa. The difference between the influences of Ne and Ar is clearly related to the difference in their chemical activities, which are defined by their electronic configurations, *i.e.* their atomic radii being 0.38 Å for Ne and 0.71 Å for Ar.

The photo-luminescence (PL) microscopy images and steady-state PL spectra acquired under ambient pressure revealed that the PL properties were strongly dependent on the type of PTM and on the maximum pressure attained. Using the dual wavelength excitation technique (Mor *et al.*, 2016) these observations, described in detail in Section S6, point to a markedly higher degree of amorphization for MAPbI<sub>3</sub> single crystals exposed to high pressure in Ar than in Ne. Thus, the optical characterization of MAPbI<sub>3</sub> supports the conclusions of the X-ray study that the large difference in the atomic radii of Ar and Ne leads to significantly different effects of high pressure on the crystallinity of MAPbI<sub>3</sub> after pressure release.

### 3.4. Influence of Ne and Ar on the methylammonium cation mobility

The role of the mobility of the MA cation is often discussed (Motta *et al.*, 2015; Ou *et al.*, 2016; Capitani *et al.*, 2016; Szafrański & Katrusiak, 2016). The high-pressure amorphization is also directly linked to this phenomenon. According to Ou *et al.* (2016), Capitani *et al.* (2016) and Szafrański & Katrusiak (2016), the strong pressure-induced interaction between the MA cations and I atoms leads to the absence of the MA periodicity, which was considered as a template for the stability of the (Pb,I)-framework. Following this interpretation, our results support the following scenarios of the influence of Ne and Ar on the MA cation behaviour. In both cases, Ne–MA and Ar–MA interactions minimize the MA mobility by fixing the position of the MA dumbbell (the log-range-ordered form of MA). In particular, this explains the absence of cubic symmetry for the high-pressure phases.

In the case of Ne–PTM, up to ~3 GPa, MA interacts with both Ne and I; that stabilizes its long-range ordering. For P >3 GPa, intensifying interaction between MA and 12 neighbouring I atoms forces this cation to lose its long-range periodicity, first partially (for 3 GPa < P < 8 GPa) then completely (for P > 8 GPa). However, the Ne–I interaction becomes sufficiently strong to stabilize the (Pb,I)-framework. This prevents amorphization and maintains the crystalline state up to 20.27 GPa. These pressure-induced Ne–I interactions remain after decompression.

In the case of Ar PTM, MA cations interact with Ar to form -I-Ar-MA-Ar- chains as Ar enters the crystal. Formation of the chains prevents strong interaction between MA and I and, consequently, stabilizes the long-range periodicity of MA. At 1.34 GPa, some of the cations still exist outside of the chains. The uncovered cations stimulate additional absorption of Ar by the crystal, and all MA cations are involved in the polymerized chains at 2.39 GPa, but some of the Ar–MA and Ar–I distances are too short. On the one hand, it points to strong MA–Ar interactions, which benefit from the competition with the MA–I ones. On the other hand, the I–Ar–MA–Ar– chains get crowded in the restricted space between the PbI<sub>6</sub> octahedra and they crush the structure. This means collapse of the structure. Despite somewhat speculative character, this scenario can explain both the small observed contribution of the crystalline phase at 2.39 GPa and the rapid irreversible amorphization upon further pressure increase.

#### 4. Conclusions

Using single-crystal synchrotron diffraction data, the crystal structure of  $CH_3NH_3PbI_3$  (MAPbI<sub>3</sub>) was studied under different pressures with noble gases, Ne and Ar, as pressure transmitting media creating hydrostatic conditions. The following main conclusions have been drawn from the study.

(i) In the case of MAPbI<sub>3</sub> compression up to 20.3 GPa, the noble gas atoms of the pressure transmitting media are not inert, but rather they form NeMAPbI<sub>3</sub> and ArMAPbI<sub>3</sub> high-pressure-induced compounds.

(ii) Ne mainly interacts with I atoms, preventing amorphization and stabilizing the high-pressure crystalline state up to 20.27 GPa, despite the migration of MA cations to non-periodic positions. This means a loss of the long-range ordering of MA within the crystal lattice. The high-pressure transformation is reversible and the Ne<sub>0.97</sub>MAPbI<sub>3</sub> compound is stable at ambient conditions after decompression.

(iii) Ar interacts with both MA and I, thus forming chains and driving their pressure-induced polymerization up to P =2.39 GPa. Compression of the (Pb, I)-framework destroys the polymerized structure and, consequently, the framework itself, initiating the irreversible and rapid amorphization of the compound.

(iv) The difference between the pressure-induced impacts of Ne and Ar is related to the difference in their atomic radii and, consequently, their propensity towards interatomic interactions in the restricted space between the  $PbI_6$  octahedra.

We believe that the findings presented can encourage the research community to conduct deeper experimental and theoretical studies of plausible chemical reactions of noble gases in the interstitial compartments of other compounds under high pressure.

#### 5. Related literature

References cited in the supporting information include: Bruce *et al.* (2011), Derenzo *et al.* (2013), Innocenzo *et al.* (2014), Klintenberg *et al.* (2003) and Wright *et al.* (2016).

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### Supporting information for article:

Pressure-induced transformation of CH3NH3Pbl3: the role of the noble-gas pressure transmitting media Alla Arakcheeva, Volodymyr Svitlyk, Eleonora Polini, Laura Henry, Dmitry Chernyshov, Andrzej Sienkiewicz, Gaétan Giriat, Anastasiia Glushkova, Marton Kollar, Bálint Náfrádi, Laszlo Forro and Endre Horváth



### 1 Influence of crystal quality on the HP-transformations of MAPbl<sub>3</sub>

1 The high-pressure transformation of the MAPbI<sub>3</sub> crystals of different quality with Ne-PTM. (a) A multiple crystal of a high mosaicity and traces of its decay. The crystal is completely amorphous at about 4 GPa and shows only a partial recrystallization after decompression. (b) Crystal of low mosaicity and without any traces of decay. A part of the crystal keeps its crystalline state up to about 20 GPa and completely recovers its crystalline state after decompression. Two light circles observed at P = 4.19 GPa appear from two amorphous fractions: the outer one is due to Ne-liquid; the inter one is to the MAPbI<sub>3</sub> amorphous fraction. At  $P \ge 7.4$  GPa, only the amorphous circle is observed since Ne becomes crystalline.

### 2 Experimental illustrations of a pressure-dependent transformation of MAPbI3 with Ar and Ne as PTM



**Figure S1** The high-pressure transformation of the good quality MAPbI<sub>3</sub> crystals with Ar-PTM. The reciprocal space sections HK0 and HK1 are shown. The Ar-liquid fraction gives a light circle well

visible at P = 0.49 and 0.98 GPa. This circle disappears at  $P \ge 1.34$  GPa due to Ar crystallization. The crystalline fraction of MAPbI<sub>3</sub> is essential at  $P \le 2.39$  GPa; its presence practically disappears at  $P \ge 3.64$  GPa. Formation of the amorphous fraction is detectable at  $P \ge 2.1$  GPa (a light circle). The increase of the circle intensity indicates the increase of the amorphous fraction volume.



**Figure S2** Details of the pressure induced phase transformations of MAPbI<sub>3</sub> with Ne as PTM. The *hk*0 (*HK*0) and *hk1* (*HK*1) planes of the reciprocal space correspond to the lattice parameters of the tetragonal (pseudo-cubic) phases. The axes *h*, *k* (*H*, *K*) and some reflections specific only for the tetragonal (pseudo-cubic) modification are underlined by blue (yellow). Superposition of the tetragonal and pseudo cubic specific reflections at P = 0.11 GPa confirms the two-phases state of the crystal. The diffraction patterns of released crystal are practically identical to those of the starting pristine crystal (space group *I*422,  $a = b \approx a_{pr}\sqrt{2} \approx 8.8$  Å and  $c \approx 2a_{pr} \approx 12.7$  Å).

### 3 Details of the crystallographic data and quality of the structure refinements

Table S1Experimental details for Ne-MAPbI3 compounds revealed at high pressure with Ne asPTM

Experiments were carried out at 293 K using Abstract diffractometer; empirical (using intensity measurements) absorption correction was applied.

	(I)	(II)	(III)	(IV)
Crystal data	_			
Chemical	$Ne_{0.42}[CH_3NH_3]PbI_3 =$	$Ne_{0.6} [CH_3NH_3]PbI_3 =$	Ne <sub>0.91</sub> [CH <sub>3</sub> NH <sub>3</sub> ]PbI <sub>3</sub>	$Ne_{1.10}[CH_3NH_3]_{0.5}PbI_3$
formula	Ne <sub>0.42</sub> MAPbI <sub>3</sub>	Ne <sub>0.6</sub> MAPbI <sub>3</sub>	= Ne <sub>0.91</sub> MAPbI <sub>3</sub>	$(CH_3NH_3)_{0.5}$ * =

				Ne <sub>1.12</sub> MA <sub>0.5</sub> PbI <sub>3</sub>
				(MA <sub>0.5</sub> )*
$M_{ m r}$	628.5	632.1	638.3	642.55
Crystal system,	Trigonal**, R-3	Trigonal**, R-3	Trigonal**, R-3	Orthorhombic, Im2m
space group				
Pressure (GPa)	0.69	1.5	2.69	4.56
a, b, c (Å)	17.3128(9),	17.0325(9),	16.7757(9),	11.435(3), 11.437(3),
	17.3128(9),	17.0325(9),	16.7757(9),	11.442(3)
	10.6019(9)	10.4338(5)	10.2267(5)	
$\alpha, \beta, \gamma(^{\circ})$	90, 90, 120	90, 90, 120	90, 90, 120	90, 90, 90
$V(\text{\AA}^3)$	2752.0(3)	2621.4(2)	2492.5(2)	1496.4(7)
Ζ	12	12	12	8
Radiation type	Synchrotron, $\lambda =$	Synchrotron, $\lambda =$	Synchrotron, $\lambda =$	Synchrotron, $\lambda =$
	0.3738 Å	0.3738 Å	0.3738 Å	0.3738 Å
Data collection		•	·	
No. of	1677, 799, 392 [ <i>I</i> >	1449, 673, 427 [ <i>I</i> >	703, 387, 239 [ <i>I</i> >	1481, 783, 269 [ <i>I</i> >
measured,	3 <b>σ</b> ( <i>I</i> )]	3σ( <i>I</i> )]	3σ( <i>I</i> )]	2σ( <i>I</i> )]
independent and				
observed				
reflections				
$R_{\rm int}$	0.078	0.051	0.060	0.119
Range of $h, k, l$	$h = -20 \rightarrow 20, k =$	$h = -16 \rightarrow 12, k =$	$h = -20 \rightarrow 10, k =$	$h = -6 \rightarrow 7, k =$
	$-14 \rightarrow 16, l = -11 \rightarrow 12$	$-20 \rightarrow 16, l = -9 \rightarrow 11$	$-2 \rightarrow 19, l = 0 \rightarrow 10$	$-10 \rightarrow 10, l = -10 \rightarrow 10$
Refinement	l	1		1
$R[F^2 > 2\sigma(F^2)],$	0.069, 0.078, 1.69	0.049, 0.059, 1.73	0.084, 0.083, 2.27	0.058, 0.073, 0.88
$wR(F^2), S$				
No. of	799	673	387	783
reflections				
No. of	44	40	40	59
parameters				
No. of restraints	0	1	1	2
H-atom	No H atoms have	No H atoms have	No H atoms have	H-atom parameters
treatment	been included into	been included into	been included into	constrained
	refinement	refinement	refinement	
$\Delta \rho_{max}, \Delta \rho_{min}$ (e	1.87, -1.68	1.00, -0.89	2.31, -1.20	0.40, -0.42
Å-3)				

	(V)	(VI)	(VII)	(VIII)
Crystal data				

Chemical	Ne <sub>1.41</sub> [CH <sub>3</sub> NH <sub>3</sub> ] <sub>0.25</sub>	Ne <sub>2.17</sub> PbI <sub>3</sub> (CH <sub>3</sub> NH <sub>3</sub> )*	Ne <sub>2.5</sub> PbI <sub>3</sub> (CH <sub>3</sub> NH <sub>3</sub> )*	$Ne_{0.97}[CH_3NH_3]PbI_3=$
formula	$PbI_3(CH_3NH_3)_{0.75}* =$	$= Ne_{2.17}PbI_3(MA)^*$	= Ne <sub>2.5</sub> PbI <sub>3</sub> (MA)*	Ne <sub>0.97</sub> MAPbI <sub>3</sub>
	Ne <sub>1.41</sub> MA <sub>0.25</sub> PbI <sub>3</sub>			
	(MA) <sub>0.75</sub> *			
$M_{ m r}$	622.9	631.6	638.4	639.3
Crystal system,	Orthorhombic, Im2m	Tetragonal, I4/mmm	Tetragonal, I4/mmm	Tetragonal, 1422
space group				
Pressure (GPa)	7.4	16.43	20.27	ambient pressure
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.196(3), 11.197(3),	10.701(5), 10.701(5),	10.538(5), 10.538(5),	8.876(1), 8.876(1),
	11.201(3)	10.622(5)	10.379(5)	12.672 1)
$\alpha, \beta, \gamma(^{\circ})$	90, 90, 90	90, 90, 90	90, 90, 90	90, 90, 90
$V(\text{\AA}^3)$	1404.2 (7)	1216.3 (8)	1152.6 (10)	998.34 (15)
Ζ	8	8	8	4
Radiation type	Synchrotron, $\lambda =$	Synchrotron, $\lambda =$	Synchrotron, $\lambda =$	Synchrotron, $\lambda =$
	0.3738 Å	0.3738 Å	0.3738 Å	0.7153 Å
Data collection				
No. of	1125, 335, 163 [ <i>I</i> >	481, 100, 39 [ <i>I</i> >	380, 78, 32 [ <i>I</i> >	3819, 1453, 1096 [ <i>I</i> >
measured,	2σ( <i>I</i> )]	2σ( <i>I</i> )]	2σ( <i>I</i> )]	3σ( <i>I</i> )]
independent and				
observed				
reflections				
R <sub>int</sub>	0.060	0.058	0.082	0.029
Range of $h, k, l$	$h = -5 \rightarrow 5, k = -8 \rightarrow 8,$	$h = -9 \rightarrow 9, k = -9 \rightarrow 9,$	$h = -8 \rightarrow 8, k = -8 \rightarrow 8,$	$h = -11 \rightarrow 11, k =$
	$l = -8 \rightarrow 8$	$l = -6 \rightarrow 5$	$l = -5 \rightarrow 5$	$-12 \rightarrow 12, l = -18 \rightarrow 18$
Refinement	ļ	1	1	ļ
$R[F^2 > 2\sigma(F^2)],$	0.057, 0.068, 0.87	0.051, 0.057, 1.44	0.043, 0.064, 1.49	0.035, 0.049, 1.73
$wR(F^2), S$				
No. of	335	100	78	1453
reflections				
No. of	34	18	18	76
parameters				
No. of restraints	1	0	0	1
H-atom	-	-	-	H-atom parameters
treatment				constrained
$\Delta \rho_{max}, \Delta \rho_{min}$ (e	0.29, -0.32	0.58, -0.60	1.06, -1.25	1.43, -0.87
Å-3)				

\* Contribution of  $MA = CH_3NH_3$  in non-localized (non-periodic) positions. \*\* The hexagonal unit cell is links to the body-centred pseudo cubic one by the transformation matrix (1-10 / 01-1 /0.5 0.5 0.5).

**Table S2**Experimental details for Ar-MAPbI3 compounds revealed at high pressure with Ar asPTM

Experiments were carried out at 293 K using Abstract diffractometer; empirical (using intensity measurements) absorption correction was applied.

	(I)	(II)		(III)	(IV)
Crystal data		•		•	•
Chemical formula	Ar <sub>0.76</sub> (CH <sub>3</sub> NH <sub>3</sub> )PbI <sub>3</sub>	Ar(CH <sub>3</sub> NH <sub>3</sub> )F	$PbI_3 =$	$Ar_{1.34}(CH_3NH_3)PbI_3 =$	Ar <sub>1.4</sub> (CH <sub>3</sub> NH <sub>3</sub> )PbI <sub>3</sub>
	= Ar <sub>0.76</sub> MAPbI <sub>3</sub>	ArMAPbI <sub>3</sub>		Ar <sub>1.34</sub> MAPbI <sub>3</sub>	= Ar <sub>1.4</sub> MAPbI <sub>3</sub>
M <sub>r</sub>	650.2	659.9		673.4	675.9
Crystal system, space	Tetragonal, P4 <sub>2</sub> bc	Tetragonal, P	$4_2 bc$	Tetragonal, P4 <sub>2</sub> bc	Orthorhombic,
group					Immm
Pressure (GPa)	0.18	0.49		0.98	1.34
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.850(5), 8.850(5),	8.7468(15),		8.7222(15),	12.1294(12),
	12.520(5)	8.7468(15),		8.7222(15),	12.1415(12),
		12.398(1)		11.9979(15)	12.1734(15)
$\alpha, \beta, \gamma(^{\circ})$	90, 90, 90	90, 90, 90		90, 90, 90	90, 90, 90
$V(Å^3)$	980.6 (9)	948.5 (2)		912.8 (2)	1792.8 (3)
Ζ	4	4		4	8
Data collection					
No. of measured,	887, 211, 95 [ <i>I</i> >	1057, 210, 99	[I >	1260, 247, 84 [ <i>I</i> >	772, 237, 104 [ <i>I</i> >
independent and	<b>3</b> σ( <i>I</i> )]	3σ( <i>I</i> )]		3σ( <i>I</i> )]	2.5o(I)]
observed reflections					
R <sub>int</sub>	0.098	0.106		0.076	0.121
Range of <i>h</i> , <i>k</i> , <i>l</i>	$h = -9 \rightarrow 9, k = -9 \rightarrow 9,$	$h = -9 \rightarrow 9, k =$	=-9→9,	$h = -10 \rightarrow 10, k =$	$h = -14 \rightarrow 15, k =$
	$l = -14 \rightarrow 14$	$l = -14 \rightarrow 14$		$-10 \rightarrow 10, l = -15 \rightarrow 14$	$-4 \rightarrow 4, l = -15 \rightarrow 14$
Refinement		•			-
$R[F^2 > 2\sigma(F^2)],$	0.049, 0.073, 1.44	0.068, 0.086,	1.80	0.079, 0.115, 1.82	0.086, 0.108, 1.40
$wR(F^2), S$					
No. of reflections	211	210		247	237
No. of parameters	28	28		28	36
No. of restraints	1	1		1	4
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	2.62, -2.36	3.78, -3.57		2.43, -2.03	0.86, -1.10
	(V)		(VI)		
Crystal data					
Chemical formula	Ar <sub>1.78</sub> (CH <sub>3</sub> NH <sub>3</sub> )PbI <sub>3</sub>	=	Ar <sub>1.75</sub> (0	$CH_3NH_3)PbI_3 = Ar_{1.75}$	MAPbI <sub>3</sub>
	Ar <sub>1.78</sub> MAPbI <sub>3</sub>				
M <sub>r</sub>	692.1		689.9		

Crystal system,	Orthorhombic, Immm	Orthorhombic, Immm
space group		
Pressure (GPa)	2.1	2.39
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.0192 (10), 12.0195 (10),	11.900 (1), 11.990 (1), 11.920 (1)
	12.0213 (10)	
$\alpha, \beta, \gamma$ (°)	90, 90, 90	90, 90, 90
$V(\text{\AA}^3)$	1736.7 (3)	1700.8 (2)
Ζ	8	8
Data collection		
No. of measured,	799, 248, 78 [ <i>I</i> > 2.5σ( <i>I</i> )]	714, 247, 46 [ <i>I</i> > 2.5σ( <i>I</i> )]
independent and		
observed reflections		
$R_{\rm int}$	0.116	0.124
Range of <i>h</i> , <i>k</i> , <i>l</i>	$h = -14 \rightarrow 14, k = -4 \rightarrow 4, l =$	$h = -14 \rightarrow 14, k = -4 \rightarrow 4, l = -14 \rightarrow 14$
	-14->14	
Refinement		
$R[F^2 > 2\sigma(F^2)],$	0.084, 0.124, 1.01	0.066, 0.144, 1.08
$wR(F^2), S$		
No. of reflections	248	247
No. of parameters	36	36
No. of restraints	4	4
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	2.16, -1.02	1.42, -1.32

### 4 Selected geometry characteristics in crystal structures of the HP transformed MAPbl<sub>3</sub>

**Table S3**Selected distances and angles in the  $PbI_3$ -framework of the HP transformed MAPbI\_3 atdifferent pressures with Ne as PMT.

Pressure,	Pb - I	dist., Å	Average Pb - I	I-Pb-I angles in	Pb-I-Pb angles
GPa			dist., Å	octahedron, deg.	between octahedra,
0.69	Pb1:	Pb2:	3.12	89.5(2) - 90.5(2)	deg. 157.4(1)
	3.131(4) ×2	3.108(6) ×6			157.9(2)
	3.111(7) ×2				
1.5	3.128(5) ×2 Pb1:	Pb2:	3.09	89.6(1) - 90.4(1)	153.84(16) ×2
	3.094(3) ×2	3.092(5) ×6			
	3.089(6) ×2				

2.69	3.091(4) ×2 Pb1:	Pb2:	3.06	89.2(4) - 90.8(4)	153.6(4)
	3.035(10) ×2	3.090(16) x 6			154.5(5)
	3.048(19) ×2				
	2.983(14) ×2				
4.56	Pb1:		3.02	72(1) - 110(1)	149(1) - 173(1)
	3.069(18)				
	2.78(2)				
	2.844(16)				
	3.074(16)				
	2.916(12)				
7.4	2.825(12) Pb1:		2.87	69(1) - 110(1)	141(2) - 168(2)
	3.135(10)				
	2.50(1)				
	3.151(15)				
	2.79(2)				
	2.81(3)				
16.43	2.86(3) Pb1:	Pb2:	2.68	82.6(4) - 97.4(4)	180.0(5) x 3
	2.481(17) ×4	2.892(17) ×4			170.7(8)
	2.900(15)	2.655(3) ×2			
20.27	2.411(15) Pb1:	Pb2:	2.62	88.4(3) - 90.3(10)	180.0(5) x 3
	2.53(2) ×4	2.74(2) ×4			177.9(8)
	2.65(2)	2.595(3) ×2			
1 atm	2.54(2) 3.160(4) ×4		3.16	89.57(8) - 90.43(4)	180.0(5) x 2
(released)	3.144(4)				166.6(1)
1 atm	3.192(4) 3.173(1) ×4		3.17	89.96(1) - 90.04(1)	180.0(5) x 2
(start)*	3.1727(7)				163.59(5)
	3.1777(7)				

\* Data were extracted from Ref. Arakcheeva et al. (2017).

**Table S4**Selected distances and angles in the PbI<sub>3</sub>-framework of the HP transformed MAPbI<sub>3</sub> atdifferent pressures with Ar as PMT.

Pressure,	Pb - I dist., Å	Average Pb - I	I-Pb-I angles in	Pb-I-Pb angles between
GPa 0.18	Pb1:	dist., Å 3.13	octahedron, deg. 89.4(9) - 90.6(9)	octahedra, deg. 176.6(8) - 180.0(5)
	3.138(14) ×2			
	3.123(14) ×2			

	3.16(5)			
0.49	3.10(5) Pb1_1:	3.12	81(1) - 99(1)	180.0(5) ×2
	3.11(5) ×4			162(2)
	3.20(8)			
0.98	3.09(9) Pb1:	3.09	79(1) - 101(1)	180.0(5) ×2
	3.21(5) ×2			158(1)
	3.07(5) ×2			
	3.03(5)			
1.34	3.97(5) 3.049(4) ×2	3.13	81.7(10) - 98.3(10)	144(1)
	3.122(7) ×2			168(1)
2.10	3.204(10) ×2 3.118(9) ×2	3.10	78.5(13) - 101.5(13)	153(1) 149.1(12)
	3.028(5) ×2			165.9(16)
2.39	3.160(7) ×2 3.023(5) ×2	3.09	79.3(14) - 100.7(14)	144.0(7) 139.7(10) - 165.2(14)
	3.07(3) ×2			
	3.175(10) ×2			

#### b Ar PTM Ne PTM а (i) Pressure (G Pa) Pressure (GPa) Released 0.7 2.7 20.3 16.3 pressure 0.18 2.4 2.50 Ne Δ 0.42 MA 1 • (MA) 0.76 1.75 0.49 G P a 1.34 G P a 2.69 G P a 20.27 G P a 2.39 G P a 1 atm Neo.91 MAPbl3 N e 1.41 M A 0.25 P b 13 N e 2.5 P b 13 N e o .96 M A P b I 3 ArMA Pbl3 Ar1.4 MAPbl3 A r 1.75 M A P b I 3 (M A )0.75 (M A) Im 2 n 14 / m m m 1422 P42bc Im m m lm m m (ii) 🔶.. M A (disordered) (ordered) (iiii) ŧ м́А ł

#### 5 Structure illustrations

**Figure S3** Typical examples of the Ne-MAPbI<sub>3</sub> and Ar-MAPbI<sub>3</sub> structures and their evolution under compression with (a) Ne and (b) Ar pressure transmitting medium (PTM). Panel (i) specifies composition and symmetry at different pressures. MA and (MA) indicate detected (long-range ordered, periodic) and undetected (non-periodic) contribution of the organic cation MA. Panel (ii) shows a representative fragment of the structure at different pressures. Panel (iii) illustrates a general

tendency of the structure evolution, which is different for Ne-MAPbI<sub>3</sub> and Ar-MAPbI<sub>3</sub>. In Ne-MAPbI<sub>3</sub>, Ne positions are close to the centres of the faces of a primitive perovskite cube. Increasing of pressure initiates an increase of their occupancies. Ne partially and randomly occupies all such positions in the released (decompressed) crystal at ambient pressure. In Ar-MAPbI<sub>3</sub>, I-Ar-MA-Ar-chains are formed at pressure of 0.18 GPa and exist up to 1 GPa. The chains are polymerized into layers (1.34 GPa) and then into framework (2.39 GPa).



**Figure S4** Evolution of the Ne-MAPbI<sub>3</sub> structures under compression and after pressure release. Panel **a** specifies a scheme of Ne positions in faces of the primitive perovskite cubic unit cell. These positions underlined by cyan squares formed by I atoms and centred by Ne. Some of the positions can be empty or partially occupied depending on pressure. Panel **b** shows a change of the crystal composition induced by pressure. In the chemical formula, *y* and (1-y) define the long-range ordered (detectable) MA and the randomly distributed (non-detectable), respectively. Panel **c** presents the shortest interatomic contacts under different pressures. Panel **d** demonstrates the main tendency of the pressure dependant structure evolution: the Ne positions, indicated in **a**, gradually increase in their occupancy. Only  $\frac{1}{3}$  of them are partially occupied under 2.69 GPa, and all of them are occupied under 20.27 GPa. Unexpectedly, all these positions are (partially) occupied in the unpacked crystal.



Figure S5 Evolution of the Ar-MAPbI<sub>3</sub> under increased pressure.



**Figure S6** Pressure dependent evolution of the I-Ar-MA-Ar interactions in the Ar-MAPbI<sub>3</sub> structures. Too short Ar - MA distances (red) appeared under 2.39 GPa point to instability of the structure, which is at amorphization.

## S1. Optical microscopy luminescence imaging and steady-state photo-luminescence (PL) measurements

To offer a faster and convenient detection of the amorphous phase, we performed photo-luminescence optical microscopy imaging and steady–state photo-luminescence (PL) measurements. While using two excitation wavelengths, 470 nm and 546 nm, we simultaneously acquired both luminescence microscopy images and collected the PL spectra. This novel methodological approach enabled us to

unambiguously elucidate the presence or absence of the amorphous phase in MAPbI<sub>3</sub> single crystals, which were formerly exposed to HP.

#### S2. Technical details

Optical microscopy luminescence imaging and steady-state photo-luminescence (PL) measurements were carried out under ambient-pressure conditions for MAPbI<sub>3</sub> single crystals that were previously pressurized with both pressure transmission media that is Ne and Ar. Similar experiments were also performed for the MAPbI<sub>3</sub> single crystals pressurized in Ne to 11.6 GPa, as well as for the intact MAPbI<sub>3</sub> single crystals (control measurements).

Specifically, the optical microscopy luminescence imaging and collection of the steady-state PL spectra were performed for MAPbI<sub>3</sub> single crystals that were formerly pressurized to 19.6 GPa and 20.27 GPa, in Ar and Ne, respectively. These studies were performed under ambient-pressure condition, *i.e.* after the pressure release and removal of the MAPbI<sub>3</sub> crystals from the DAC. Moreover, the steady-state PL spectra were also collected for the MAPbI<sub>3</sub> single crystals located in a fully assembled DAC and pressurized in Ne to 11.6 GPa. The latter measurements were then repeated under ambient-pressure conditions, *i.e.* after the pressure release and removal of the MAPbI<sub>3</sub> single crystals located for the MAPbI<sub>3</sub> crystals from the DAC.

The steady-state PL spectra were collected with using a custom-designed setup combining an inverted biological epi-fluorescent microscope (TC5500, Meiji Techno, Japan) with a compact spectro-fluorometer (USB 2000+XR, Ocean Optics Inc., USA). To gather optical images of the studied MAPbI<sub>3</sub> crystals, a digital non-cooled CCD camera (Infinity 2, Lumenera Co., Ottawa, Canada) was used. Prior to perform measurements, the MAPbI<sub>3</sub> single crystals were positioned on the standard glass microscope slides (75 mm by 26 mm, 1 mm thick). A tiny amount of silicon grease was used to immobilize MAPbI<sub>3</sub> crystals on microscope slides.

In this study, the steady-state PL spectra were recorded upon illumination with two excitation wavelengths,  $\lambda_{exc}$ , of 470 nm and 546 nm. These two excitation wavelengths were filtered out from the emission spectrum of the microscope's Mercury vapor 100-W lamp by implementing two dedicated sets of Meiji Techno filters, *i.e.* 11001v2 Blue and 11002v2 Green, for  $\lambda_{exc}$  of 470 nm and 546 nm, respectively (Mor *et al.*, 2016).

The control optical microscopy luminescence imaging and steady-state PL measurements were performed under ambient-pressure condition on the pristine MAPbI<sub>3</sub> single crystals originating from the same batch as the crystals exposed to high-pressure.

## S3. Ambient-pressure luminescence optical microscopy and steady-state PL measurements performed on the intact MAPbl<sub>3</sub> single crystals (control measurements)

The luminescence microscopy imaging and PL measurements were performed on the control MAPbI<sub>3</sub> single crystals, which were from the same batch as those used in the high-pressure experiments and also had roughly similar volumes, being of ~4.5x10<sup>-5</sup> µL. Specifically, the control photoluminescence images were acquired under illumination with two excitation wavelengths,  $\lambda_{exc}$ , of 470 nm and 546 nm. Moreover, in parallel to microscopic imaging, our experimental setup enabled also to simultaneously collect the corresponding steady-state photo-luminescence (PL) spectra.



**Figure S7** Typical microscopic images and steady-state PL spectra acquired under ambient-pressure conditions for a control single crystal of MAPbI<sub>3</sub>: (a) the image obtained under visible light; (b) the image recorded upon excitation at  $\lambda_{exc} = 546$  nm; (c) the image recorded upon excitation at  $\lambda_{exc} = 470$  nm; and (d) the corresponding steady-state PL spectra obtained upon excitation at  $\lambda_{exc} = 470$  nm (blue trace) and  $\lambda_{exc} = 546$  nm (green trace).

The typical fluorescence microscopy images and steady-state PL spectra acquired for a control MAPbI<sub>3</sub> single crystal at two excitation wavelengths, 546 nm and 470 nm, are shown in Fig. 8.

As can be seen in Fig. 8b, upon excitation of the control crystal at 546 nm, the CCD camera picks up strong red photoluminescence corresponding to the short-wavelength wing of the characteristic photoemission of MAPbI<sub>3</sub>, which usually exhibits a luminescence peak centered at ~770 nm. As expected, this red photoluminescence, although definitely weaker, is also present in the image obtained upon excitation at 470 nm (Fig. 8c). The strongly emitting individual bright spots, which can be seen in Fig. 8b, correspond to enhanced luminescence extraction from the crystal fragments directly touching the microscope glass slide. The steady-state PL spectra, acquired simultaneously with microscopic imaging, are shown in Fig. 8d. These spectra are depicted by the blue and green traces, for excitation wavelengths at 470 nm and 546 nm, respectively.

Taken together, the fluorescence microscopy images and PL spectra acquired for the control single crystal confirm the presence of a pure crystalline phase of MAPbI<sub>3</sub>. It is also worth noting that the herein observed red-shifted emission peak of the characteristic photoluminescence of MAPbI<sub>3</sub>,  $\lambda_{em max}$ , from the typically reported value of ~770 nm (for polycrystalline MAPbI<sub>3</sub> films) to ~790 nm, is fully consistent with earlier reports suggesting the red-shifted PL peak position (along with the red-shifted optical absorption edge) for larger crystallite sizes (D'Innocenzo *et al.*, 2014).

# S4. Ambient-pressure luminescence optical microscopy and steady-state PL measurements of MAPbl₃ single crystals formerly pressurized to 19.6 GPa in Ar



**Figure S8** Microscopic images and steady-state PL spectra recorded under ambient-pressure conditions for the MAPbI<sub>3</sub> single crystal that was pressurized previously to 19.6 GPa in Ar: (a) the image obtained under visible light, (b) the image recorded upon excitation at 470 nm, and (c) the image recorded upon excitation at 546 nm; (d) the corresponding steady-state PL spectra obtained upon excitation at 470 nm (blue trace) and 546 nm (green trace). The long-pass filter-dependent onsets of PL spectra acquired under two excitation wavelengths, 470 nm and 546 nm, are indicated by the vertical broken blue and green lines, respectively.

The visible-light microscopic image recorded at ambient-pressure conditions for a single crystal of MAPbI<sub>3</sub>, which was previously pressurized to 19.6 GPa in Ar, is shown in FIG. S9a. The photoluminescence images of this crystal, acquired upon excitation at 470 nm and 546 nm, are shown in Fig. S9b and Fig. S9c, respectively. As can be seen, on excitation at 470 nm, the crystal emits a strong yellow-green photo-emission (Fig. S9b), whereas on excitation at 546 nm, the CCD camera

picks up a rather weak red photo-emission (Fig. S9c). The corresponding PL spectra, acquired for this MAPbI<sub>3</sub> crystal under the excitation with both wavelengths, are shown in Fig. S9d.

The yellow-green photo-emission observed in the microscopic image acquired on excitation at 470 nm (Fig. S9b), as well as the corresponding broad PL spectrum with a stronger peak at ~540 nm and a weaker one at ~775 nm (the blue trace in Fig. S9d), point to the presence of an intermediate amorphous phase. In particular, the yellow-green emission peaking at ~540 nm can tentatively be ascribed to the rhombohedral lead iodide, PbI<sub>2</sub>, having the optical band-gap of ~2.55 eV (Klintenberg *et al.*, 2003). This broad and asymmetric PL peak is usually associated with donor-acceptor pair transitions in PbI<sub>2</sub> (Derenzo *et al.*, 2013). The weaker photo-luminescence feature, centered at ~775 nm, can definitely be associated with the tetragonal phase of MAPbI<sub>3</sub> (Wright *et al.*, 2016). As can also be seen, this PL peak gets substantially stronger on excitation at 546 nm (the green trace in Fig. S9d). We infer that a much weaker intensity of the PL peak centered at ~775 nm upon excitation at 470 nm, as compared to the excitation at 546 nm, is related to the presence of the above-mentioned amorphous phase, which filters out and attenuates the excitation wavelength ( $\lambda_{exc} = 470$  nm).

Interestingly, even after prolonged illumination with both excitation wavelengths, *i.e.*  $\lambda_{exc}$  of 470 nm and 546 nm, we did not observed any significant alterations in the PL signal intensity. Notwithstanding, both PL signals, excited either by 470 nm or 546 nm and centered at ~770 nm, were very weak, thus pointing to a high degree of amorphization of the MAPbI<sub>3</sub> single crystal, which was formerly compressed with Ar to 19.6 GPa.

## S5. Steady-state PL measurements of MAPbl₃ single crystals pressurized in Ne to 11.6 GPa (PL measurements performed for the crystals located in the pressurized DAC)

The steady-state PL spectra of MAPbI<sub>3</sub> single crystals pressurized with Ne to 11.6 GPa were collected through the diamond culet of a fully-assembled DAC, which was positioned on the sample stage of our inverted epi-fluorescent TC5500 microscope. A long-working-distance objective (Meiji, F10, WD=7.5 mm) was used to acquire the PL spectra from the MAPbI<sub>3</sub> single crystals located in the sample compartment of the DAC.

The actual location of two MAPbI<sub>3</sub> single crystals within the sample compartment of the DAC is shown in Fig. S10a. As can be seen, the two MAPbI<sub>3</sub> crystals were loaded along with two ruby crystals (pressure gauges). The corresponding steady-state PL spectra, acquired on excitation at two wavelengths, *i.e.* with  $\lambda_{exc}$  of 470 nm and 546 nm, are displayed in Fig. S10b.



**Figure S9** (a) The optical microscopy image of the sample compartment of the DAC pressurized with Ne to 11.6 GPa showing the location of two MAPbI<sub>3</sub> single crystals loaded along with two ruby crystals (pressure gauges). (b) The steady-state PL spectra collected through the diamond culet of the DAC under the optical excitation with two wavelengths,  $\lambda_{exc}$ , 470 nm (blue trace) and 546 nm (green trace). The sharp luminescence feature at 698.5 nm is related to the luminescence of Cr<sup>3+</sup> ions in ruby crystals.

As can be seen in Fig. S10b, the characteristic photoluminescence of MAPbI<sub>3</sub> centered at ~770 nm is totally missing in both PL spectra. Instead, the only observable luminescence peak in this wavelength-range is a narrow photo-emission feature at 698.5 nm, which is related to the photo-luminescence of  $Cr^{3+}$  atoms in ruby. Being pressure-dependent, this luminescence peak of  $Cr^{3+}$  is red-shifted by 4.5 nm as reference to its position at the ambient pressure, thus confirming the high-pressure conditions (P = 11.6 GPa) in the sample compartment.

The observed broadened and asymmetric photo-luminescence feature at shorter wavelengths, peaking at ~545 nm (on excitation at 470 nm), can tentatively be associated with the rhombohedral lead iodide, PbI<sub>2</sub>, having the optical band-gap of ~2.55 eV (the blue trace in Fig. S10b) (Klintenberg *et al.*, 2003). In fact, such broad and asymmetric PL emission is usually attributed to donor-acceptor pair transitions in PbI<sub>2</sub> (Derenzo *et al.*, 2013). The intrinsic fluorescence of the diamond culet can also contribute to the observed photo-luminescence in this wavelength range (the blue trace in Fig. S10b), since it is well established that natural and artificially-grown diamonds reveal photo-luminescent features at 540 - 560 nm (Bruce et al., 2011).

Similarly, a slightly stronger PL signal, peaking at 598 nm under excitation with  $\lambda_{exc} = 546$  nm (the green trace in Fig. S10b), can be associated with the combined contributions of the photo-luminescent response of PbI<sub>2</sub> and luminescent defects in diamond. The latter PL spectrum is partially cut-off on the short-wavelength side (at 590 nm) by the microscope long-pass filters.

It has to be stressed that the herein reported total suppression of the characteristic photo-luminescence of MAPbI<sub>3</sub> centered at  $\sim$ 770 nm for crystals pressurized in Ne to  $\sim$ 11.6 GPa corroborates earlier reports concerning the high-pressure induced changes in the crystalline structure and photo-luminescence properties of this metal-organic perovskite (Capitani et al., 2016).

## S6. Ambient-pressure steady-state PL measurements on a single crystal of MAPbl<sub>3</sub> formerly pressurized in Ne to 11.6 GPa

After the pressure release, the steady-state PL spectra were collected at ambient-pressure conditions for the MAPbI<sub>3</sub> crystal, which formerly was pressurized to 11.6 GPa in Ne. As mentioned above, under high-pressure conditions, this crystal did not reveal any photo-luminescence. In contrast, after the pressure release, a gradual recovery of the characteristic luminescence of MAPbI<sub>3</sub>, peaking at  $\sim$ 770 nm, was observed for this crystal. The microscopic image of the MAPbI<sub>3</sub> single crystal, which was formerly pressurized to 11.6 GPa in Ne is shown in Fig. S11.



**Figure S10** The visible-light ambient-pressure optical microscopy image of the MAPbI<sub>3</sub> single crystal formerly pressurized in the DAC to11.6 GPa with Ne.

The time-dependent gradual recovery of the characteristic luminescence at  $\sim$ 770 nm for this MAPbI<sub>3</sub> crystal at ambient-pressure conditions and upon excitation with two wavelengths, 546 nm and 470 nm, is displayed in Fig. S12.



**Figure S11** The time-dependent gradual recovery of the characteristic luminescence at ~770 nm for a single crystal of MAPbI<sub>3</sub> formerly pressurized to 11.6 GPa in Ne. The luminescence microscopy images recorded for the single crystal of MAPbI<sub>3</sub> on excitation at 546 nm for the progressively elongating illumination times: 0 min (**a**), 148 min (**d**) and 258 min (**g**). The luminescence microscopy images recorded for the single crystal of MAPbI<sub>3</sub> upon excitation at 470 nm for the progressively elongating illumination times: 0 min (**b**), 144 min (**e**) and 256 min (**h**). The corresponding PL spectra acquired upon excitation at 546 nm and 470 nm for the progressively elongating illumination times: 0 min (**b**), 144 min (**c**) and 256 min (**h**). The corresponding PL spectra acquired upon excitation at 546 nm and 470 nm for the progressively elongating illumination times: 0 min (**b**).

As shown in Fig. S12, upon excitation at 546 nm and 470 nm, the characteristic luminescence band of MAPbI<sub>3</sub> peaking at ~770 nm increased gradually with progressively elongating illumination times. The luminescence microscopy images shown in this figure were recorded in the beginning of the experiment (Fig. S12 a & b) and after 148 min (Fig. S12 d & e) and 258 min (Fig. S12 g & h) of illumination. It is worth mentioning that the CCD camera used in our experimental setup was only able to detect the short-wavelength portion of the NIR emission of MAPbI<sub>3</sub>. In contrast, the PL spectra, acquired simultaneously (after roughly the same time-lapse intervals), provided the whole spectral information on the time-evolution of the characteristic photo-luminescence of MAPbI<sub>3</sub>. These PL spectra, are shown in Fig. S12 c, f & i. As can be seen, after the subsequent illumination intervals, the marked overall growth of luminescence was also accompanied by a shift of the maximum-intensity wavelength from 778 nm (in the beginning of the experiment) to 789 nm (after 258 min of exposure to the excitation light). Similar red-shifted luminescence of MAPbI<sub>3</sub> has been reported earlier and associated with increasing crystal or grain sizes (D'Innocenzo *et al.*, 2014).

Summarizing, at ambient-pressure conditions, the MAPbI<sub>3</sub> single crystal, which was formerly pressurized with Ne to 11.6 GPa, recovered the characteristic photo-luminescence emission around 770 nm, which gradually increased for longer exposure times. Therefore, the herein reported time-dependent increase of the photo-luminescence, accompanied also by the spectral red-shift, can tentatively be explained by a gradual recovery of the ordered crystalline phase of the MAPbI<sub>3</sub>. It is worth noting that such behavior was not observed at ambient-pressure conditions for the MAPbI<sub>3</sub> crystal, which was formerly pressurized to 19.6 GPa in Ar. In the latter case, even after prolonged illumination, the PL intensity at 770 nm did not markedly changed and remained low. Moreover, the crystal compressed in Ar conserved a relatively strong luminescence at shorter wavelengths, which could tentatively be ascribed to the presence of an intermediate (amorphous / PbI<sub>2</sub>-like) phase.

## S7. Ambient-pressure steady-state PL measurements on a single MAPbl<sub>3</sub> crystal formerly compressed to 20.27 GPa in Ne (i.e. the MAPbl<sub>3</sub> crystal attached to a thin glass capillary)

The optical microscopy images and steady-state PL spectra were acquired at ambient pressure conditions for a single crystal of MAPbI<sub>3</sub>, which was formerly pressurized with Ne to 20.27 GPa. After the pressure release and prior to PL measurements, this crystal was attached to a thin glass capillary to perform ambient-pressure XRD studies. Therefore, to avoid any further damage, the subsequent optical imaging and PL measurements were performed for this MAPbI<sub>3</sub> crystal also attached to the thin glass capillary.

The visible-light microscopic image of the MAPbI<sub>3</sub> crystal attached to a glass capillary is shown in Fig. S13.



**Figure S12** The visible-light optical microscopy image of the MAPbI<sub>3</sub> single crystal mounted on a thin glass capillary. Formerly, this MAPbI<sub>3</sub> single crystal was compressed in Ne to 20.27 GPa and subsequently, after the pressure release, it was used at ambient-pressure for the further characterization by XRD, optical microscopy imaging and PL measurements.



**Figure S13** Ambient-pressure optical imaging and PL measurements performed for the MAPbI<sub>3</sub> crystal formerly compressed to 20.27 GPa in Ne. The luminescence microscopy images recorded on excitation at 546 nm in the beginning of the experiment (**a**) and after 160 min of illumination (**d**). The luminescence microscopy images recorded on excitation at 470 nm in the beginning of the experiment (**b**) and after 160 min of illumination (**e**). The steady-state PL spectra recorded upon excitation at 546 nm and 470 nm recorded in the beginning of the experiment (**c**) and after 160 min of illumination (**f**).

As shown in Fig. S14 a & c, in the beginning of the experiment, the characteristic luminescence of MAPbI<sub>3</sub> peaking at ~770 nm was very weak upon excitation with both 546 nm and 470 nm wavelengths. In contrast, as can be seen in Fig. S14 b & c, under the excitation with 470 nm wavelength, the yellow-green portion of the luminescence was relatively strong, thus pointing to the presence of the intermediate phase.

As it is depicted in Fig. S14 d & f, under the prolonged illumination (of 160 min), the intensity of the characteristic luminescence of MAPbI<sub>3</sub> at ~770 nm markedly increased, thus reaching ~11 times higher level than in the beginning of the experiment. Interestingly, the yellow-green portion of the luminescence, peaking at ~540 nm, increased much less, *i.e.* by ~20% only. These observations suggest that, although during the prolonged illumination the volume of the MAPbI<sub>3</sub> crystalline phase has been largely recovered, the volume of the amorphous phase (luminescent at ~ 540 nm) remained essentially constant.

As can also been seen in Fig. S14 c & f, the characteristic luminescence of MAPbI<sub>3</sub> at  $\sim$ 770 nm changed its spectral shape as a function of illumination time. In particular, the wavelength of the maximum emission shifted from 774 nm in the beginning of the experiment to  $\sim$ 800 nm after 160 min of illumination. A similar red-shift of the PL spectra has recently been reported in the context of the growing sizes of MAPbI<sub>3</sub> crystallites (D'Innocenzo et al., 2014). Therefore, the red-shift of the PL

spectra at  $\sim$ 770 nm observed herein can be ascribed to the progressively growing volume of the MAPbI<sub>3</sub> crystalline phase.

Overall, the ambient-pressure microscopy imaging and PL measurements performed for the MAPbI<sub>3</sub> crystal compressed in Ne to 20.27 GPa point to a much higher damage of the crystal structure than for the MAPbI<sub>3</sub> crystal, which was formerly compressed in Ne to a lower pressure, *i.e.* of 11.6 GPa. In particular, this large structural damage manifests itself by the presence of a pronounced yellow-green luminescence (peaking at ~540 nm), whereas for the MAPbI<sub>3</sub> crystal formerly compressed to 11.6 GPa its level was markedly lower. Moreover, this type of a broad emission around 540 nm was also observed for the MAPbI<sub>3</sub> single crystal formerly pressurized in Ar to 19.6 GPa and was tentatively associated with the presence of an amorphous phase. It is also worth noting that this broad emission around 540 nm was totally absent in PL spectra acquired for the intact MAPbI<sub>3</sub> crystals.

## S8. Conclusions concerning the optical microscopy luminescence imaging and steady-state PL measurements

Our methodological approach, consisting of using two excitation wavelengths, *i.e.*  $\lambda_{exc}$  of 470 nm and 546 nm, to acquire both luminescence microscopy images and to collect steady-state PL spectra enabled us to elucidate, in a relatively simple way, the presence or absence of an intermediate (amorphous) phase in MAPbI<sub>3</sub> single crystals that were formerly exposed to high-hydrostatic pressures. Specifically, by switching excitation wavelength from 546 nm (2.27 eV) to 470 nm (2.64 eV), we could preferentially excite the amorphous fractions, containing, most presumably, the amorphous lead iodide (PbI<sub>2</sub>) and thus having the optical band-gap of ~2.55 eV that is higher than the optical band-gap of MAPbI<sub>3</sub> (1.65 eV).

In particular, upon excitation at 470 nm, we observed a relatively strong yellow-green emission peaking at ~540 nm for a single crystal of MAPbI<sub>3</sub>, which was formerly pressurized to 19.6 GPa in Ar. This broad and asymmetric PL emission, occurring at shorter wavelengths, could tentatively be associated to a high degree of amorphization and the presence of  $PbI_2$ -containing phase.

In contrast, the MAPbI<sub>3</sub> single crystals, which were formerly exposed to high-hydrostatic pressures of 11.6 GPa and 20.27 GPa in Ne, did not reveal such strong emission at shorter wavelengths, thus suggesting a definitely lower degree of the structural damage. Clearly, the acquired fluorescence microscopy images and corresponding steady-state PL spectra pointed to a higher degree of pressure-induced damage for the MAPbI<sub>3</sub> single crystal pressurized to 20.27 GPa than for 11.6 GPa. Notwithstanding, after prolonged illumination, the MAPbI<sub>3</sub> single crystals formerly exposed to high-hydrostatic pressures in Ne to 11.6 GPa and 20.27 GPa largely recovered the characteristic photo-luminescence of MAPbI<sub>3</sub> centred at ~770 nm. Interestingly, the gradual overall growth of the luminescence intensity was also accompanied by a shift of the maximum-intensity wavelength from ~775 nm to ~800 nm, in the beginning and in the end of the experiment, respectively. Such red-

shifted luminescence can be attributed to a progressive recovery (volumetric increase) of the pristine fractions of the MAPbI<sub>3</sub> crystal.

As expected, the characteristic photo-luminescence of MAPbI<sub>3</sub> centred at  $\sim$ 770 nm was totally suppressed for the MAPbI<sub>3</sub> single crystals pressurized in Ne to  $\sim$ 11.6 GPa. This latter observation is consistent with previously published data on the high-pressure behaviour of this metal-organic perovskite.

Taken together, the fluorescence microscopy images and steady-state PL spectra acquired at ambientpressure conditions performed on the MAPbI<sub>3</sub> single crystals, formerly exposed to high-hydrostatic pressures, revealed photo-luminescence properties that were strongly dependent on the type of the pressure transmitting media (Ne or Ar) and on the maximum pressure attained. Specifically, our results point to a much high degree of amorphization of MAPbI<sub>3</sub> single crystals exposed to highhydrostatic pressure in Ar.