Locking of Methylammonium by Pressure-Enhanced H-Bonding in $(\text{CH}_3\text{NH}_3)\text{PbBr}_3$ Hybrid PerovskiteF. Capitani,^{*,†,‡} C. Marini,[‡] S. Caramazza,[§] P. Dore,[§] A. Pisanu,^{||} L. Malavasi,^{||} L. Nataf,[†] F. Baudelet,[†] J.-B. Brubach,[†] P. Roy,[†] and P. Postorino[§][†]Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, 91192 Gif-sur-Yvette, France[‡]CELLS-ALBA, Carretera B.P. 1413, Cerdanyola del Valles 08290, Spain[§]Department of Physics, "Sapienza" University of Rome, P. le Aldo Moro 2, 00185 Rome, Italy^{||}Department of Chemistry and INSTM, University of Pavia, Via Taramelli 16, 27100 Pavia, Italy

Supporting Information

ABSTRACT: Organo-lead halide perovskites are nowadays considered to be an emerging photovoltaic material. It is clear that the peculiar hybrid nature of this class of materials is central for their outstanding optical and transport properties. However, the role of the organic cation and its interplay with the inorganic framework remains elusive. To get insight into the interactions at play, high-pressure Raman, infrared, and X-ray absorption spectroscopy measurements were performed on MAPbBr_3 ($\text{MA} = \text{CH}_3\text{NH}_3^+$). Since lattice compression allows for a fine-tuning of the organic/inorganic interaction, we were able to follow the pressure evolution of the MA dynamics within the PbBr_6 cage and identify different phases. From a MA dynamical disordered configuration, the system enters at first a cation ordered phase and, at higher pressure, a static disordered MA phase. Data analysis points at H-bonding as the driving force for molecular reorientation. Since the MA dynamics directly influence the formation of polarons in hybrid perovskites and their ferroelectric properties, the present results provide the basis for the understanding of the transport mechanisms at the core of the outstanding properties of this class of materials.

INTRODUCTION

Lead halide perovskites nowadays represent the most promising photovoltaic materials for the production of low-cost, high-performance solar cells.^{1,2} For this class of materials of general formula ABX_3 ($\text{B} = \text{Pb}, \text{Sn}$ and $\text{X} = \text{Cl}, \text{Br}, \text{I}$), an inorganic cage of BX_6 octahedra encloses an organic cation at the A-site (typically methylammonium $\text{MA} = \text{CH}_3\text{NH}_3^+$). The hybrid nature of such compounds, that is, the combination of a robust albeit flexible inorganic skeleton with an organic cation with variable shape and composition, is the basis of their outstanding properties as sunlight absorber. The inorganic framework mostly determines the electronic band structure and thus the optical properties.³ Size, shape, and orientation of the organic cation at the A-site, as well as the extent of the H–X interaction, have direct effects on the surrounding cage of octahedra and thus, in turn, on the electronic/optical properties of the system.^{3–9} A band gap narrowing on increasing the cation size was observed in recently published papers.^{4,10–12} For MAPbI_3 , theoretical calculations have shown that when MA is oriented along different crystallographic directions, the nature of the band gap changes from direct to indirect causing a modified gap value.⁷

MA-based compounds, namely, MAPbCl_3 , MAPbBr_3 , and MAPbI_3 , show similar sequences of structural phases on decreasing temperature.¹³ From the high-temperature cubic phase with freely rotating MA cations, these compounds enter a

lower-symmetry tetragonal phase and finally a low-temperature orthorhombic phase with the MA cations fixed at oriented ordered positions.^{6,13–16} The role of H-bonds formed between MA and the surrounding halogen atoms was recently highlighted in theoretical studies.^{11,17,18} The onset of strong H-bonds freezes the rotation of the MA cations and induces a modification of the surrounding PbX_6 octahedra. The MA order/disorder transition has a deep impact also on other critical properties; in particular, an effective charge screening in the MA dynamical disordered phase was invoked to justify the exceptionally long carrier lifetimes and diffusion lengths observed.¹⁹ The rotation of the dipolar cations creates a sort of *cloaking field* that screens the carriers from scattering by defects and phonons, which drives a polaron-based transport mechanism.¹⁹

Applying hydrostatic pressure is another way to fine-tune the complex organic/inorganic interaction.^{20–22} In addition to a few early works,^{23,24} the effects of pressure on the optical, electronic, and structural properties of MAPbX_3 perovskites were investigated only very recently.^{25–33} In MAPbI_3 and MAPbBr_3 , common features were observed on compressing the lattice: a phase transition toward a lower-symmetry phase in the

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0–1 GPa pressure range, and a reversible amorphization process that takes place above ~ 3 GPa and is completed at higher pressures.^{23,25,27–30} The whole scenario is however not clearly established: Wang et al. observed a cubic to orthorhombic transition at 1.8 GPa in MAPbBr₃,²⁵ but no transitions in the 1.0–2.7 GPa range were reported in a neutron diffraction experiment²³ and in a more recent X-ray diffraction (XRD) study.²⁷ Little is known also about the cation order/disorder transitions under pressure. XRD studies, which are more sensitive to the heavy inorganic cage than to the light organic cation, can hardly provide direct information about the MA ordering, and a neutron diffraction experiment failed to find an ordered phase of deuterated MAPbBr₃ under pressure.²³ Vibrational spectroscopy, in contrast, may provide relevant information as it is sensitive to both organic (at intermediate and high frequency) and inorganic (at very low frequency) parts. Moreover, by probing the C–H and N–H vibrations of the MA cation, vibrational spectroscopy is also an effective tool to investigate the effect of pressure on the H-bonding network.³⁴

Finally, external pressure can also be used to simulate and understand the effects of chemical pressure and strain^{35,36} which have been exploited to tune the optical properties of a hybrid perovskite film.^{37–39}

Here, we report on high-pressure (HP) spectroscopy study of the hybrid perovskite MAPbBr₃. In order to investigate the behavior of the organic cation and the H-bond network under pressure, we exploited Raman, infrared (IR), and X-ray absorption (XAS) spectroscopies. In particular, the evolution of hydrogen bonding under pressure was investigated through the study of the C–H / N–H vibrational modes and of the near-edge XAS signal (XANES).

RESULTS AND DISCUSSION

Raman and IR spectra are shown in Figure 1 at four significant pressures over the 20–400 and 50–400 cm^{−1} ranges, respectively. Spectroscopic data collected at all the pressures are reported in the Supporting Information (SI) in Figures S1–S3.

At $P = 0.0$ GPa (ambient pressure), Raman spectra are characterized by a major, featureless band centered at zero Raman shift, and a weaker one around 150 cm^{−1}. At ambient conditions, MAPbBr₃ is expected to be in the cubic phase $Pm\bar{3}m$, with freely rotating MA molecules,^{15,40} and in principle no Raman activity should be observed over this frequency range.^{41,42} The MA dynamic disorder drives structural fluctuations making the Pb–Br vibrations Raman active as well as MA librations/translations typical of this low-frequency range.^{43,44} The same argument holds for the torsional mode of MA, theoretically silent^{44–46} but here assigned to the well-defined peak at ~ 325 cm^{−1} (see Figure 1b).

The far-IR (FIR) spectrum at ambient conditions shows a broad band below 200 cm^{−1} (see Figure 1c). Interference fringes in the background signal, due to multiple reflections between the two internal diamond faces, prevent clearly distinguishing specific spectral features, although the overall signal is consistent with other experimental reports.^{44,47} The absence of other IR peaks up to 400 cm^{−1} shows that the disorder-activated Raman torsional mode is IR silent; i.e., the torsional motion of MA does not induce any appreciable modification of the molecular dipole moment.

On increasing pressure, the low-frequency Raman signal becomes more and more structured (see Figure S1), and new

Figure 1. Low-frequency Raman (panels a and b) and infrared (c) spectra of MAPbBr₃ at four selected pressures representative of the different high-pressure phases of the system. (d) Pictorial representation of the three MA dynamical regimes within the inorganic cage (full lines) on increasing the pressure.

peaks appear in the spectra at 1.9 and 3.5 GPa (see Figure 1a). Above 4 GPa, a broad featureless band replaces the well-defined spectral features. It is worth noticing that the torsional mode at 325 cm^{−1} vanishes at the highest pressures. A similar sequence of spectral changes can be identified in the FIR spectra although its interpretation is not straightforward.

Notice, in particular, the rise of the signal between 50 and 100 cm^{−1} above 1 GPa in a fashion similar to what was observed in the Raman spectra. At 3.2 GPa a large peak is clearly observed at ~ 106 cm^{−1} which, on further increasing the pressure, shifts toward higher energies, reduces its intensity, and slightly broadens. From the whole set of spectroscopic data, and especially from Raman, a series of phase transitions is now clear. If the Raman spectra at ambient pressure, at ~ 1.9 GPa, and at ~ 5.2 GPa are representatives of the cubic phases $Pm\bar{3}m$ and $Im\bar{3}$ and the amorphous phase, respectively,^{23–25,27} the spectrum at ~ 3.5 GPa clearly points out the existence of another structural phase at intermediate pressures. This is spectroscopic evidence of the presence of the debated

Figure 2. Raman (a, b, c panels) and infrared (d, e, f) spectra of MAPbBr₃ over the *fingerprint* frequency region, i.e., where the internal vibrations of methylammonium appear, at four selected pressures representative of the different high-pressure phases of the system. Black asterisks mark new peaks appearing in the orthorhombic phase at intermediate pressure.

orthorhombic *Pnma* phase observed by Wang et al. at about the same pressure values.²⁵

It is worth noticing that the spectrum at 3.5 GPa shows well-resolved peaks over the 25–150 cm^{−1} region, strongly suggesting the ordering of the MA molecules in the HP orthorhombic phase (as schematically represented in Figure 1d). In fact, similar low-frequency Raman spectra present sharp, well-defined peaks, at *P* = 0.0 GPa and *T* < 149 K (see Figure S4). In this case, an orthorhombic *Pnma* phase, with ordered, locked MA cations, was proposed.^{15,40} We point out that even though an orthorhombic structure is assumed for both the low-temperature (at *P* = 0.0 GPa) and the HP (at *T* = 300 K) phases, the differences between their Raman spectra indicate a different arrangement of MA cations (compare Figure 1a with Figure S4). Therefore, before reaching the MA ordered HP orthorhombic phase, the MA free rotation in the first cubic phase becomes locked around fixed axes at slightly higher pressure in the second cubic phase.

MA dynamic disorder in the cubic phases, as well as MA static disorder in the HP amorphous phase, shows broad spectral features in the low-frequency region of the Raman spectrum. However, as mentioned above, the MA torsional mode around 325 cm^{−1} (see Figure 1b) disappears on entering the amorphous phase. This suggests that the molecular torsional motion is strongly hindered by volume compression and, possibly, by strengthened H-bonding at HP, with this picture being compatible with statically disordered molecules (see Figure 1d). In this respect, we have to consider the shape of the organic cation, which can induce asymmetric distortions of the octahedral cage. The interaction among the MA molecules is thus mediated by the inorganic cage, which, in turn, is modified by the dynamics and/or the orientation of the organic cation.

This idea of a compression driven molecular ordering through a strong organic–inorganic interplay is also corroborated

by a recent theoretical work based on *ab initio* molecular dynamics.⁴⁸ Indeed, Ghosh and co-workers showed that, in a mixed-cation hybrid perovskite, the motion of the organic ion is restricted and even “locked” by the chemical pressure resulting from the substitution of the CH(NH₂)₂⁺ (formamidinium) with a smaller Cs⁺ ion.⁴⁸

Further insight on the HP behavior of MA is obtained through the analysis of the Raman and IR spectra in the *fingerprint* frequency range (800–3400 cm^{−1}),^{44–46,49} which provides an exhaustive description of the vibrational dynamics. Since MA is noncentrosymmetric, most of the peaks are both Raman and IR active although with different relative intensities. Raman and IR spectra measured at representative pressures are shown in Figure 2.

The vibrational spectra over the 800–1200 cm^{−1} range (Figure 2a,d) at 0 GPa present two main peaks at ~910 and ~970 cm^{−1}, ascribed to an N–H₃ rocking and a C–N stretching mode, respectively, whose relative intensities are swapped between Raman and IR. As the pressure is increased over 0–2.3 GPa, a general frequency hardening is observed, as well as a clear splitting of the C–N peak when entering the orthorhombic phase (see Figure S2 in the SI). The peak splitting is quite evident at 3.5 GPa in Figure 2a, and since the C–N vibration is nondegenerated, it can be ascribed to a MA reorientation which modifies the local surrounding environment.⁵⁰ Further peak splitting is found also at higher frequencies in the spectral region of C–H/N–H bending (1400–1700 cm^{−1} in Figure 2b,e) and stretching modes (2700–3400 cm^{−1} in Figure 2c,f).

On further increasing the pressure above 4.0 GPa, the system enters the amorphous phase where narrow Lorentzian-shaped peaks are replaced by broad and Gaussian-shaped peaks (see the spectra in Figure 2 at 5.2 GPa), reflecting a statistical distribution of the vibrational frequencies of orientationally disordered MA molecules.

The detailed pressure dependence of the observed spectral features can be found in the SI (see Figure S5–S6), although Figure 2 already shows that different peaks exhibit a different pressure response. In particular, as the pressure increases, only the C–N stretching mode (970 cm^{-1} at 0 GPa) shows an approximately linear frequency hardening (panels a and d). In contrast, the vibrational modes involving H atoms show diverse evolutions with pressure, with a clear frequency softening for C–H/N–H bending modes (panels b and e) and complex pressure dependence for the frequencies of C–H/N–H stretching modes (panels c and f).

These vibrational modes provide direct information on the evolution of H-bonding, which defines the organic–inorganic interplay.^{7,17,18,23,40} For instance, in the low-temperature orthorhombic phase, tilting and deformation of the PbBr_6 octahedra occur to optimize the N–H $\cdots$ Br hydrogen bonding, inducing the orientational ordering of MA.^{23,40} Octahedral tilting and deformation were also reported at HP,^{25,27} and thus, a prominent role of H-bonding in the compressed systems can be anticipated.

The pressure dependence of the average vibrational frequency of the Raman active C–H and N–H stretching modes (i.e., those shown in Figure 2c and Figure S6) is reported in Figure 3. It slightly increases along the two low-

Figure 3. Pressure dependence of the average C–H and N–H Raman stretching frequencies. Different background colors show the pressure ranges of the different structural phases identified.

pressure cubic phases up to 2.4 GPa, whereas a clear downshift on entering the orthorhombic phase occurs. This evolution suggests a major H-bond network rearrangement. In particular, the average frequency decreases over the whole pressure range of the orthorhombic phase, i.e., up to 4.0 GPa. This clearly indicates that the strengthening of the H-bonding accompanies the MA ordering process characteristic of this phase, similarly to the low-temperature behavior of MAPbBr_3 and as also pointed out by theoretical calculations.⁴⁸ Above 4 GPa, i.e., in the amorphous phase, the average C–H and N–H frequency increases as a function of pressure indicating that the disorder of MA ions weakens the extended network of H-bonds.

In order to get further insight into the processes induced by lattice compression, pressure dependent XAS spectra at the Br K-edge and at the Pb L-edge were collected. XAS allowed us to probe independently the Pb and Br empty density of states, i.e., to reveal the relevant states composing the conduction band. XANES spectra are shown in Figure 4 where the effect of pressure is significant at the Br edge, albeit still detectable also at the Pb edge. In the dipole approximation, the Pb L3-XAS

Figure 4. XAS spectra of MAPbBr_3 as a function of pressure at the Pb L3-edge (a) and Br K-edge (b). XAS difference spectra are shown in the insets. The pale-yellow area indicates the region where the integral of the difference spectrum was evaluated. Integrated area as a function of pressure is report in panel c for the Pb L3-edge (black $\circ$) and for the Br K-edge (blue $\bullet$). The same color code as in the previous figures is used to indicate the pressure ranges of different phases.

spectrum corresponds to the electron excitation from the deep $2p_{3/2}$ states into outer empty nd states ($n > 5$). $5d$ states are completely filled (Pb valence is +2), and the absorption edge appears smooth, without strong resonance, except for the peak at 13 091 eV labeled as A (see Figure 4a). Lattice compression progressively moves the A peak at higher energy and decreases its spectral weight. Similarly, at the Br K-edge, the A and B peaks at 13 650 and 13 675 eV (Figure 4b) show a progressive shift toward high energy together with a remarkable intensity loss. According to calculations performed in similar compounds, A and B features can be associated with the $1s \rightarrow 4p$ unbounding transition, i.e., to π^* empty orbitals transitions.⁵¹ The pressure behavior of A and B implies an increase of the “metallic” character of HP MAPbBr_3 , since an increase of delocalized electrons modifies the distribution of electronic empty states around the Fermi energy in both Pb and Br atoms.

To understand the electronic processes induced by lattice compression, we first calculated the difference between the spectra collected at a given P and at $P = 0$, i.e., $\mu(E)_{P=0} - \mu(E)_P$ (shown in the insets in Figure 4a,b), and then the integrated areas over the energy regions corresponding to the A-feature (yellow shadow areas in the same insets). The latter ones are shown in Figure 4c as a function of pressure. Notably, beside a scale factor, both Pb and Br edges show the same evolution with pressure. This is not surprising since the difference in electronegativity between Pb and Br is quite low (2.33 and 2.96, respectively); i.e., Pb s and Br p orbitals experience a strong hybridization which characterizes the valence band of the system, whereas the conduction band has mainly Pb p character.²⁶

Between 0 and ~ 1 GPa, the values of the A and B integrals rapidly increase. In the same pressure range, Pb–Br bond distances shrink leading to enhancing the Pb s and Br p orbital coupling in the valence band and to narrowing the band gap.³² As a result, the “metallic” character of the MAPbBr₃ increases. The A and B features thus track this process, which ends with a discontinuity corresponding to the phase transition into the second cubic phase. Above ~ 1 GPa, the Pb–Br distance is further reduced, and the Pb–Br–Pb angle, constant at lower pressure, gets smaller.³² The behavior of the Pb–Br–Pb angle thus accounts for the absence of relevant changes in the XANES (constant value of the integrals of the A features) in the cubic and orthorhombic phases. Finally, when the system enters the amorphous phase above ~ 4 GPa, the A and B feature integrals increase again.

EXAFS spectra, collected at the Br K-edge and reported in Supporting Information, do not show a remarkable difference as a function of pressure (see Figure S9), supporting the idea that the observed change is mainly due to electronic structure modification induced by lattice compression. More specifically, we can conclude that both Pb and Br atoms experience a broadening of their bands, with consequential smearing of the empty states resonance, causing an increase of delocalized electrons. This increased delocalization could lead to the appearance of a metallic state in MAPbBr₃ at much higher pressures, as recently observed in MAPbI₃ at 60 GPa.³³ Finally, it is important to note that pressure mostly affects the signal from the Br K-edge than the Pb L3 (notice the two different vertical scales in Figure 4c). Since the Br absorber is physically closer to the organic molecule and considered the N–H $\cdots$ Br H-bonds, we hypothesize that the excess of charge on the Br atoms originates from the MA ions acting as a charge reservoir in MAPbBr₃.

CONCLUSIONS

In conclusion, we investigated the pressure behavior of the prototypical hybrid perovskite MAPbBr₃ up to 10 GPa, paying particular attention to the effect of lattice compression on the MA cation and its interaction with the surrounding inorganic framework. Results obtained with Raman, infrared, and X-ray absorption spectroscopies allow us to identify four different phases over the 0–10 GPa pressure range. Raman and infrared vibrational spectra clearly show a MA dynamically disordered phase at ambient pressure, and a MA locked phase between 2.3 and 4 GPa. The cation ordering process is driven by the onset of strong pressure-induced hydrogen bonding, as consistently revealed by the low-frequency response, the vibrational modes involving H atoms, and the Br XANES signal. In the HP regime, above 4 GPa, the system enters a new phase

characterized by statically disordered cations. In summary, the ensemble of the organic molecules follows a sequence of transitions under pressure which drive the system from a liquid-like phase to a crystalline phase and finally to an amorphous phase. Bearing in mind that molecular orientation directly affects polaronic, ferroelectric, and electronic properties, our results provide the essential experimental basis for modeling the organic–inorganic interplay, as well as for a deeper knowledge of the transport mechanisms at the core of the outstanding properties of hybrid perovskites as light absorbers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b11461.

Experimental methods, additional figures showing all the Raman and IR spectra, Raman spectra at low temperatures, details of data analysis, and EXAFS spectra at high pressure (PDF)

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Notes

The authors declare no competing financial interest.

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