Intrinsic Thermal Instability of Methylammonium Lead Trihalide Perovskite

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Organolead halide perovskites currently are the new front-runners as light absorbers in hybrid solar cells, as they combine efficiencies passing already 20% with deposition temperatures below 100 °C and cheap solution-based fabrication routes. Long-term stability remains a major obstacle for application on an industrial scale. Here, it is demonstrated that significant decomposition effects already occur during annealing of a methylammonium lead triiodide perovskite at 85 °C even in inert atmosphere thus violating international standards. The observed behavior supports the view of currently used perovskite materials as soft matter systems with low formation energies, thus representing a major bottleneck for their application, especially in countries with high average temperatures. This result can trigger a broader search for new perovskite families with improved thermal stability.

1. Introduction

There are three main determinants for the large-scale viability of a photovoltaic technology on the consumer market: efficiency, cost, and lifetime. In this respect, silicon technology has provided the best compromise so far. Since their introduction in the 1950s, silicon solar cells have been extremely well studied and rigorously optimized, leading up to a current lab-scale efficiency record of ≈25% (single junction) and a guaranteed module lifetime of 25 years.[1] Even though the price per watt-peak has decreased to below 1 USD, the achievement of global grid parity is still a hurdle. Cheaper thin film technologies have thus been developed in recent years, such as organic or dye-sensitized solar cells. Unfortunately, enhancing their operational stability is still a major challenge. Furthermore, record efficiencies of around 12% do not allow to compete with silicon solar cells yet. A recently discovered alternative is the metal-organic halide perovskite solar cell which, on an extremely short time scale, has been established as the most important new candidate for next generation photovoltaics.[2–8] High absorption coefficients combined with high charge carrier mobilities and diffusion lengths, and solution processability are only a few of the many desirable features that render perovskites the potential new front-runner materials for thin film photovoltaics.[2,6–8] Despite (certified) efficiencies passing 20% already[9] the remaining bottleneck for the viability of perovskite solar cells on a larger scale is again stability: here, highest efficiencies have been reported for the methyl ammonium (MA)-based compound MAPbI₃, which is prone to degradation by humidity due to the hygroscopic nature of the alkylammonium cation present in the unit cell.[10] In this case, a proper encapsulation of a solar cell could help to avoid any contact with humidity[11] (also by hydrophobic top contacts[12,13] or UV radiation.[11,14])

One very important issue not properly addressed yet is the thermal stability of the perovskite material itself: here, according to International Standards (IEC 61646 climatic chamber tests), long-term stability at 85 °C (representing an elevated temperature on a roof on a hot summer day) is required in order to compete with the silicon-based technology. As 85 °C is in the generally applied range of deposition temperatures (60–100 °C),[2,15–17] it could be speculated that structural transformations might be initiated at 85 °C already, as diffusion coefficients of the constituents must be large, close to the formation temperature. On the one hand, thermogravimetric analysis (TGA) of MAPbI₃ showed that the crystal structure is stable up to 300 °C, but quickly decomposes above this temperature due to the fragmentation of the CH₃NH₃⁺ component.[18] On the other hand, it has been pointed out that this organic–inorganic hybrid material structurally belongs to the class of soft matter[19] and, consequently, should have a large response function to small external perturbations such as, e.g., a temperature increase. Here, we will...
demonstrate that significant structural changes already occur during annealing of MAPbI$_3$ at 85 °C in different atmospheres (pure nitrogen, pure oxygen, and ambient atmosphere) thus identifying a serious bottleneck for applying this new material.

2. Results and Discussion

In order to have a first clue about the thermal stability of the perovskite material at the microscopic level, structural optimizations were performed from first principles within density functional theory (DFT). Calculations, see the Supporting Information for computational details, were carried out to evaluate the formation energy of MAPbI$_3$ in its tetragonal phase$^{[20]}$ from the most stable PbI$_2$ and methyl ammonium iodide (MAI) crystalline phases. We calculated a formation energy of 0.11–0.14 eV per unit cell (4 MAPbI$_3$ units), depending on whether spin–orbit coupling and dispersion corrections were used, see Table S1 (Supporting Information). The rather stable formation energy value with variations in the level of theory is in line with previous results$^{[21–23]}$ pointing to values in the range 0.1–0.3 eV. These values are definitely much lower than those identified for a series of perovskite oxides screened for optimal solar light capture of comparable band gap,$^{[24]}$ suggesting the soft matter nature of MAPbI$_3$. As the average thermal energy of 0.093 eV estimated for 85 °C (assuming six degrees of freedom) is rather close to this formation energy, instabilities of individual unit cells upon annealing to such temperatures can be expected resulting in their decomposition with time.

Experimentally, in order to discriminate between degradation of the perovskite itself versus other layers in the device stack via electrical measurements (e.g., impedance spectroscopy) of complete devices is a rather challenging task. Therefore, we investigate the morphological, optical, chemical, and electrical properties of perovskite layers in semifinished solar cells. Recently, we reported the successful preparation of highly reproducible perovskite solar cells deposited in a sandwich architecture from a 3:1 precursor of CH$_3$NH$_3$I (MAI) and PbCl$_2$ in dimethylsulfoxide (DMSO), followed by a thermal treatment at 100 °C (for more details: see the Supporting Information). We confirmed the absence of Cl in these films by X-ray photoelectron spectroscopy (XPS), (see Figure S1, Supporting Information) and emphasize that the term MAPbI$_3$–Cl refers only to the method of synthesis and not the outcome (since no Cl is left behind in the perovskite). Accordingly, MAPbI$_3$ is used as the general term in this paper.

Figure 2 shows scanning electron microscopy (SEM) images of a fresh perovskite film on indium tin oxide (ITO)/TiO$_2$ (Figure 2a), and after annealing in the dark for 24 h at 85 °C in pure dry N$_2$ (Figure 2b), pure dry O$_2$ (Figure 2c), and ambient atmosphere with ≈50% relative humidity (Figure 2d), respectively. It is reasonable to assume that these conditions are negligibly detrimental for the ITO and TiO$_2$ that form the flat scaffold for the perovskite.$^{[42–44]}$ Contrary to what one might expect, the sample that was heated in N$_2$ already shows additional morphological features in the form of speckles and some short needles lying on top of the perovskite, suggesting an initial trace of degradation (Figure 2b). In the case of heating in O$_2$, all the additional features have grown into needles, and their abundance is much higher. The needles’ increased aspect ratio suggests that they are crystalline entities with a preferential growth direction, surface segregated from the topmost region of the perovskite film during annealing in N$_2$ or O$_2$ atmosphere. The sample that was heated in ambient atmosphere exhibits a significant structural change, where the original morphology is only marginally recognizable, now dominated by platelet-like, grainy structures, pointing to a more pronounced crystallization of the degradation-induced features. These initial results suggest that the perovskite can degrade of the other layers and interfaces in complete solar cells. Since, in this case, the perovskite is unprotected by a hole-transport material and metal electrode, this semifinished cell configuration could be regarded as a benchmark for the worst-case degradation scenario. Perovskite films were prepared by spincoating a 3:1 precursor of CH$_3$NH$_3$I (MAI) and PbCl$_2$ in dimethylsulfoxide (DMSO), followed by a thermal treatment at 100 °C (for more details: see the Supporting Information).
be converted into its degradation product(s) by an increased temperature of 85 °C as the only stress factor and that the degradation rate is influenced by the atmosphere in which the degradation took place.

From the X-ray diffraction (XRD) measurements in Figure 3a it is clear that the obvious initial morphological changes when heating in N2 and O2 are not directly reflected in the corresponding diffractograms. It is only for the sample degraded in ambient environment, where the degradation is much more evolved, that the perovskite-related peaks at scattering angles 2θ = 14.1°, 24.5°, and 43.3° have disappeared and the peaks at 12.7°, 52.4°, and 38.7°, have emerged, corresponding to the presence of PbI2 and to a lesser extent I2, respectively. This finding points to a transformation from CH3NH3PbI3 to PbI2 with loss of CH3NH3I. [11] The absence of PbI2 and I2 in the diffractogram of the N2 and O2 heated samples, together with the self-evident observation of grainy features in the corresponding SEM images, again suggests that the latter reside on top of the perovskite and represent only a small volume fraction as compared to the entire perovskite film. This is confirmed by results from the optical measurements in Figure 3. The bulk optical absorption (Figure 3a) of samples degraded in O2 and N2 is virtually unchanged compared to the pristine case, whereas the (grazing incidence, thus more surface sensitive) photoluminescence curves (Figure 3b) show a much reduced bandgap luminescence, together with the emergence of a peak at 510 nm that signals the presence of PbI2. This is further corroborated by low-loss Electron Energy Loss Spectroscopy (EELS) measurements (Figure S2, Supporting Information). In contrast, the ambient-degraded sample does exhibit both, a clearly decreased total absorption, with a distinct shoulder arising at 510 nm, and the lowest bandgap luminescence of all samples, proving that the degradation process has penetrated much deeper into this film compared to the N2 and O2 degraded films.

To provide a more solid judgment on the so far observed phenomena, we now present a combined surface and cross-sectional visualization study, employing conductive atomic force microscopy (C-AFM) and scanning transmission electron microscopy (STEM) using high-angle annular dark field (HAADF) cross-section transmission electron microscopy (TEM). Figure 4 shows topography images (left column) and their corresponding current maps (right column) for the same set of samples as presented in Figure 2. Inspecting the current maps closely, it becomes apparent that the regions where grainy features appear in the topography image upon degradation show up as well-defined dark areas in the current maps and are therefore not contributing to the electrical current. This is especially well expressed in the N2 and O2 treated samples and again supports the idea that these features are in fact (poorly conducting) PbI2 crystals. Confirmation hereof is provided by the bottom left image in Figure 5, where such grain is visible in cross section (highlighted oblong structure). Its relative Pb/I ratio (determined by energy dispersive X-ray (EDX) analysis) compared to unaffected perovskite regions suggests it to be in
fact PbI₂ (1.5× as much Pb w.r.t. I in the grain, compared to the bulk perovskite matrix).

For the sample degraded in ambient atmosphere, additional discernable regions in the topography image give rise to dark (current-less) areas in the current map, which can be the result of multiple causes, as will be demonstrated in the following.

Figure 5 comprises cross-sectional STEM-HAADF images of solar cells based on either a pristine or degraded perovskite layers annealed for 24 h at 85 °C in different atmospheres. In the pristine case, all the layers are stacked neatly on top of one another, whereas for degraded samples additional morphological phenomena occur. In the extreme case of annealing in air, the perovskite film is governed by spot-like structures as shown in Figure 5 (bottom right) which, using EDX analysis, can be identified as regions with increased Pb/I atomic ratio (see Figure S3, Supporting Information). Additionally, in some locations, the perovskite film appears to be delaminated from the base TiO₂ layer, thus impeding top-down charge transfer and again leading to regions with decreased electrical current. Delamination effects are not observed for samples annealed in molecular N₂ or O₂, the latter ones reveal the beginning of the formation of spot-like structures representing inhomogeneities within the perovskite film that might act as (still low density, but unwanted) scattering centers for photo-induced charge carriers during operation of the solar cell.

To obtain a more in-depth understanding of the mechanism behind the observed degradation in the previous section, XPS measurements were carried out. The chemical signature of the degradation processes was unraveled by core level scans of the most important elements (C, N, Pb, and I) for each degraded sample. The C1s core level of the pristine sample (Figure 6 left side, black curve) contains two contributions, one at higher binding energy (286.7 eV) that represents the C–N bond found in the MAI cation, and one at lower binding energy (285.3 eV; C–C, C–H) that is attributed to a small amount of adsorbed hydrocarbons as a result of ex situ preparation of the film. Upon heating the film in ambient atmosphere for different time periods, the C–N related peak gradually shrinks in favor of the hydrocarbon peak, which points to a conversion of C–N bound carbon to adventitious type carbon. The corresponding peak shift can result from the hydrogen in the ambient atmosphere that reduces the methylammonium or from the formation of a hydrate product.[45] Coinciding with the disappearance of C–N bonds, the N1s core level intensity (Figure 6 center panel, black curve) is systematically decreasing, suggesting the emission of nitrogen from the sample surface into the atmosphere. We turn our attention now towards the Pb4f core level spectra (Figure 6, right panel). Previously, we speculated a small trace of elemental Pb (Pb⁰, 136.9 eV) could contribute to the electrical conduction in the perovskite.[25] Now we find...
that the perovskite, as freshly deposited on a TiO$_2$ layer (black curve in Figure 6, right panel), does not contain any Pb$^{(0)}$. Lead in the neutral state now appears during annealing in ambient atmosphere as a result of degradation/decomposition of unit cells within the surface region. Consequently, the Pb$^{(0)}$ found earlier very likely was a degradation product induced by (unintentional) humidity rather than a dopant built into the perovskite lattice during preparation. It is worth to point out that the absence of Pb$^{(0)}$ in our new experiments evidences that its presence in the previous experiments is not due to radiation damage induced by the exposure to X-rays during our photoemission experiments, in clear contrast to earlier speculations.$^{[46]}$

The morphological manifestation of the Pb$^{(0)}$ component can be derived from the STEM-HAADF image (Figure 5): Small white structures can be distinguished inside the film after annealing in air, having a Pb/I ratio which is up to 2.5 times higher than the average ratio found in their surroundings (as determined by EDX, see Figure S3, Supporting Information). Since the brightness in STEM-HAADF images is proportional to the average Z (atomic number) of the materials under investigation, this finding—together with the detection of Pb$^{(0)}$—points to a high likelihood of the bright spots being metallic Pb clusters, which is supported by prior observations.$^{[47]}$

Returning to the chemical analysis and focusing on the sample that was degraded in dry O$_2$ conditions, it is immediately clear that the same processes are occurring as in case of ambient atmosphere: the C–N perovskite peak makes a conversion into lower binding energy carbon compounds (Figure 6a, bottom blue curve), corroborated by the disappearance of the N1s component in Figure 6b (bottom blue curve). Also a Pb$^{(0)}$ component is again arising, albeit to a much lesser extent than in the ambient case. Finally, the C1s and N1s core level spectra of the sample degraded in N$_2$ atmosphere (upper blue curves in Figure 6a,b) again show a similar trend as in the former cases, but the conversion is clearly very much slowed down; still much of the original C–N contribution and corresponding N1s component at 401 eV are present. As in the O$_2$ case, the Pb$^{(0)}$ component is only marginally present after 24 h of thermal stress, but rises substantially after 120 h.

Summarizing the chemical analysis, we can draw three main conclusions: (i) The perovskite is not only disintegrating because of the hydrophilicity of MAI (thereby breaking up the crystal structure), the MAI is actually decomposing by reacting with oxygen and water, as follows from the conversion to low binding energy carbon species and the disappearance of nitrogen. (ii) Even in the absence of oxygen and water, the perovskite is disintegrating, and so are its building blocks. The MAI is decomposing in the same fashion as in the presence of oxygen and water, though at a much slower rate. This clearly points to the fact that the perovskite tends to be unstable at 85 °C. (iii) Contrary to common belief, not all Pb$^{(2+)}$ is spent in the form of PbI$_2$ upon degradation, as evidenced by an increased contribution at the Pb$^{(0)}$ energy position. Since all carbonated Pb compounds occur at higher binding energies, and as derived from EDX analysis of cross-sectional images, the most plausible explanation is that metallic (in the sense of elemental) Pb clusters are formed upon degradation, even when executed in the dark.$^{[47,48]}$ The considerably increased peak at the Pb$^{(0)}$ position for degradation in ambient atmosphere compared to the N$_2$ and O$_2$ case indicates that water is a catalyst in the conversion of Pb$^{(2+)}$ into metallic Pb.

Next we address the impact of perovskite degradation on the performance of corresponding solar cells. Photovoltaic parameters of solar cells based on perovskite layers (subjected to 85 °C in identical atmospheric conditions as discussed before) are shown in Figure 7. Bearing in mind the drastic changes seen in the XPS analysis, the corresponding degraded perovskite layers still seem to perform relatively well in solar cells: The layers that were degraded in N$_2$ and O$_2$ still retain 93% and 78% of the reference efficiency, respectively, and even the most degraded layer that was heated in ambient atmosphere shows more than a quarter of the reference cell's efficiency. A slight nuance is appropriate here, based upon the above morphological investigation: The perovskite layers are not homogeneously degraded and the obviously more exposed topmost part of the films will exhibit the largest extent of degradation. This, together with the consideration that XPS is mainly sensitive to the topmost 5–10 nm of the film (and thus magnifies the observed phenomena in that region), explains why the degradation seems...
more dramatic from the chemical analysis than from the evaluation of the photovoltaic parameters. It is interesting to notice that the open circuit voltage ($V_{oc}$) is not too much influenced by the degradation, while the reduced short circuit current ($J_{sc}$) and fill factor (FF) are affecting the final performance much more. Even though the optical density of the degraded films is still well comparable to the pristine case (see Figure 3b), $J_{sc}$ of the corresponding solar cells decreases severely. This can be attributed to the increased resistance and associated recombination events near the interface between the perovskite and the hole conductor on top, again as a consequence of the inhomogeneous degradation of the perovskite film. Moreover, delamination of severely degraded perovskite layers from the base TiO$_2$ layer as seen in Figure 5 will also impede proper charge transfer to this electrode in that particular region. Although the area of the zero-current regions as measured by C-AFM (Figure 4, right column) is in rough proportion with the severity of the degradation and the resulting photovoltaic performance, the exact area fraction that is still conducting is not directly proportional to $J_{sc}$. This is, however, conceivable because of unaffected parts of perovskite being capped by a more degraded (thus less or not conductive) top layer.

From our results, it is clear that there is a stability issue of MAPbI$_3$ at temperatures comparable to its typical formation temperature. This is possibly less detrimental in regions of lower latitudes (N-America, Europe and a large part of Asia) but represents a considerable problem in regions with high insolation and high operating temperature near the equator, where peak module temperatures reaching 85 °C are to be expected on a daily basis. Fortunately, strategies to meet the requirements for stability at higher operating temperatures are already underway. It has been shown, for example, that two perovskites of the same family can be combined to enhance the lattice stability of the whole (and at the same time improve the performance). Alternatively, perovskites based on different elements than Pb and alkylammonium derivatives (though still exhibiting the latter’s favorable photovoltaic characteristics) are being identified that could also provide access to more rigid, thermally stable perovskite families.

3. Conclusion

In conclusion, we have investigated the thermal stability of MAPbI$_3$ perovskite layers in different environmental conditions from a morphological, electronic and chemical point of view. The final verdict is that this type of perovskite is not intrinsically stable while heating to temperatures comparable to the higher range of operational temperatures in full sunlight (85 °C). The unit cell of the perovskite breaks down not only due to humidity but also due to thermal instability of its constituents (which are partially volatile species), thereby confirming the soft matter character of this new class of light absorbers. Both the Pb-based and the organic compounds of the perovskite disintegrate to form other species that lead to a loss of its desirable photovoltaic and conductive properties. These results are an important message in view of further development of the photovoltaic perovskite technology: Even though in our work the perovskite was fully exposed upon degradation (accelerating the corresponding effects compared to a finished device) it is clear that mere encapsulation of solar modules based on the currently popular perovskites will not be sufficient to guarantee their long-term stability. While the current methyl ammonium lead iodide based cells are a very useful platform to acquire expertise, methods are needed to stabilize their crystal structure if they are ever to be employed as large-scale energy harvesters. Alternatively, other perovskites could be developed with comparable photovoltaic properties, yet with better intrinsic stability, eventually to supersede the current generation of perovskites.

4. Experimental Section

ITO substrates (15 Ω sq$^{-1}$) were cleaned by sonication in soap solution, water, acetone, and isopropanol. A previously reported 0.127 μ TiO$_2$ nanoparticle dispersion was spincoated on top.$^{[50]}$ The samples were then transferred to a N$_2$-filled glovebox (<1 ppm O$_2$ and H$_2$O). A 600 mg mL$^{-1}$ precursor of MAI and PbCl$_2$ (3:1 ratio) was prepared in DMSO and spincoated on the TiO$_2$ layer. A gradual heat treatment was then carried out, from room temperature to 100 °C at a rate of 1 °C min$^{-1}$, followed by a 60-min dwell at 100 °C (= “pristine”). Part of the samples was then subjected for the desired time to a temperature of 85 °C in different atmospheres, in the dark, to induce different levels of degradation. The samples to be heated in N$_2$ were put on a hotplate in the glovebox. The samples to be heated in ambient atmosphere were put on a petri dish in a furnace outside the glovebox. The samples to be heated in pure oxygen atmosphere were first placed inside a small vacuum chamber that was evacuated to <1 mbar and flushed with pure oxygen several times, prior to putting the chamber inside the furnace.

The samples that were intended for the fabrication of solar cells were placed back inside the glovebox after degradation and coated with a thin layer of poly-3-hexylthiophene (P3HT). A gold contact of 110 nm thickness was then evaporated through a shadow mask at a pressure of 1 × 10$^{-6}$ mbar to complete the devices. It was chosen not to subject the entire solar cells to thermal stress in order to isolate as much as possible the degradation of the perovskite itself, to avoid influences from capping.
the perovskite during degradation, and to obtain a comparable level of degradation compared to the samples used for other characterization.

IV-characterization was performed in N2 at room temperature under AM1.5 of 100 mW cm\(^{-2}\). Illumination with a Newport Oriel Class A model 91195A solar simulator, using a black mask to delineate the device area. The morphology of the degraded perovskite layers was investigated on a FEI Quanta 200FEG-SEM. XRD was measured with a Siemens D-5000 diffractometer with Cu Kα1 radiation. Chemical analysis was carried out on a commercial electron spectrometer (PHI-5600L), with an X-ray source providing monochromatized Al-Kα1 photons (1486.6 eV).

Optical absorption measurements were acquired on a Varian Cary UV–vis spectrometer. Photoluminescence spectra were taken with a Horiba-Jobin Yvon Fluorolog-3 device, with an excitation wavelength of 450 nm. Optical absorption measurements were acquired on a Varian Cary UV–vis spectrometer. Photoluminescence spectra were taken with a Horiba-Jobin Yvon Fluorolog-3 device, with an excitation wavelength of 450 nm. A Bruker Multimode 8 AFM with a V series controller was used for the conductive AFM measurements, employing Pt/Ir coated Si tips with a quoted force constant of 0.4 N m\(^{-1}\). The deflection setpoint was kept at 0.3 V to both ensure proper contact with the surface while keeping sample damage to a minimum. The samples were imaged both at a positive sample bias of 0.3 V. All measurements were done inside a N2-filled glovebox.

The degraded and pristine solar cells were transferred from Hasselt to Antwerp in a sealed container that was only opened inside the glove box. The sample was then transferred inside the glove box into a Kammrath&Weiss Gmbh transfer module together with the Focused Ion Beam (FIB) copper support grid which possesses a one way valve that does not allow gas inside the chamber and then transferred inside the FIB (FEI Helios 650). The box could then be opened only when the vacuum inside the FIB chamber was higher than the one inside the box. The FIB sample is then prepared in the traditional way. After the FIB lamella was prepared, the box was closed with the same vacuum as the FIB inner chamber and then the vacuum containing box was transported back inside the glove box. Using a special vacuum system, the box was then opened inside the glove box and the FIB sample was transferred into a Gatan double-tilt vacuum transfer holder for TEM investigation. The vacuum transfer holder was then inserted inside a FEI Titan 60-300 microscope equipped with an X-FEG high brightness electron source, a probe Cs corrector, a Super-X 4-quadrant EDX detector and a Gatan GIF Enfina electron energy loss (EEL) spectrometer. The microscope was operated at 120 kV in Scanning TEM mode with a low electron dose to avoid electron-induced damage to the perovskite. Imaging was performed with a 21 mrad convergence angle and collection of all electrons in the range 46–160 mrad for high angle annular dark field (HAADF). EDX and monochromated core-loss and low-loss EELS measurements were performed with a beam current of \(-50\) pA.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was financially supported by the Bijzonder Onderzoeksfonds (BOF, Hasselt University), the Fonds voor Wetenschappelijk Onderzoek (FWO) within the Odysseus program, and the Interreg project Organext. B.C. and A.E. are postdoctoral research fellows of FWO. The authors thank Bart Ruttens for supporting the XRD measurements. J.V. acknowledges funding from the Geconcerteerde Onderzoeksacties (GOA) project “Solarpaint” of the University of Antwerp and the FWO project G.0044.13N “Charge ordering.”

Received: March 8, 2015
Revised: April 20, 2015
Published online: