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On the environmental stability of methylammonium lead/tin halide
(CH3NH3Pb(Sn)X3) perovskites

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[Introduction] Scientists categorize methylammonium lead/tin trihalides as possible potential candidates for the third-generation of photovoltaic solar cells. They are represented by the chemical formula CH3NH3Pb(Sn)X3 (X = Cl, Br, I). They are soft nanomaterials, which are a class of hybrid minerals formed of an unusual mixing of two different ionic species, the CH3NH3+ organic cation and the [Pb(Sn)X3]2− inorganic anion, which are the key ingredients for the building block. The above formula belongs to the ABX3 perovskite family; the most common one in this family is discovered to be CaTiO3. Clearly, the formulations above possess structural similarities that explain why the mixture comprising the lead or tin trihalides and the methylammonium are referred to as organic-inorganic hybrid perovskites. Notable is their extraordinary mechanical and technological breakthroughs for which they have gone viral in academics, as well as in the solar sector today.1 For instance, the halide perovskites display large optical (photo) absorption coefficients (> 16 mm−1). They carry giant static dielectric constants ranging between 60 and 70, low exciton binding energies approximately close to 16 meV at low temperatures, exceptional minority carrier lifetimes close to 280 ns, long electron and hole diffusion lengths up to 175 microns, high charge carrier mobilities (< 100 cm2/Vs), and very low effective masses of electrons and holes (viz. tetragonal: 0.197 vs. 0.364; orthorhombic: 0.239 vs. 0.357 m∗), excellent for transport.

An attribute exposing the halide perovskites to scientific communities is their photovoltaic conversion efficiency (PCE). (The term efficiency refers a fraction of sunlight energy converted to the electrical energy via the photovoltaic technology.) The National Renewable Energy Laboratory (NREL) certified PCE ranges up to 22.1%, reported early this year.2 This is indeed a fantastic improvement compared not only to the prior value of 3.8% reported for the first time in 2009,3 but also to the crystalline silicon solar cells that have taken decades to reach a PCE somewhat closer to the above value. It is recently showed that when the mixed cesium cation lead mixed-halide perovskite tedium silicon solar cells combine with the 19%-efficient silicon solar cell, it would result in the feasibility of achieving an efficiency of conversion even greater than 25%.4 Nevertheless, an obvious feature that lifts the perovskite materials to a top level lies in a measurable property called optical band gap energy. It is tunable in the 1.5 to 3.1 eV range, with a value of < 1.6 eV being recommended for device performance. The featured characteristics mentioned above, together with their excellent transport properties, might explain why the halide perovskites do have propitious potentials to serve as p–n type semiconductor junction (photo)diodes. Nonetheless, many researchers are currently ongoing in this field to identify factors influencing the chemico-technological improvement of the PCE, the origins of anomalous hysteresis in the current–voltage characteristics, and the origins of the ferroelectricity, etc., observed for the highest efficient lead iodide perovskite. In contrary, several other researchers are involved to explore factors responsible explaining the observed air and moisture instabilities of the CH3NH3Pb(Sn)X3 perovskite films. Whilst a number of experimental observations on the latter topic have led to diverse views, there is almost no theoretical attempt placed to insight into the chemical properties of the ashydate perovskites in water (H2O). Herein, we report the electronic structure, bonding energy, molecular band gap, and electron density of the perovskite types upon its exposure to moisture forms mono- and di-hydrates, CH3NH3PbI3•H2O and (CH3NH3PbI3)2•H2O, respectively, as the integral parts of the degradation mechanism. And that the introduction of the H2O molecule into the geometry of the lead iodide perovskite not only result in the widening of the band gap of the material, but also changes its surface morphology.

Oppositely, a recent experimental investigation of Manesh et al. demands that the CH3NH3PbI3 film is only a little affected upon its exposure to humidity.5 Its major degradation occurs when it is exposed with photon dose. This conclusion was drawn after the MAPbI3 pristine films were exposed separately to both dark and light. It made the film to result in more intense degradation despite their ~7 times shorter shelf-life (~ 100 h) in light relative to that observed in the dark (~ 600 h). Contrariwise, when the authors exposed the CH3NH3PbI3 film to photon dose in dark, they did not observe the presence of the PbI2, suggesting the film was not degraded. However, the authors did observe a change in the color of the film from dark to light brown, which they recognized as a consequence of structural variations in the film. Note that when the 5, 10, and 20 wt% films of the latter type were placed in light, they underwent significant degradation especially in the interface region formed between the TiO2 electron transport layer and the perovskite films, consistent with observations of others.6–9 These were contradictory with those the pristine films exposed to similar environments, which resulted in complete degradation of the films leading to PbI2. Consequently, these results propagate the degradation of both the film types mainly by photon dose under humid condition.

Nevertheless, there are about three crystallographic structures reported for hydrated CH3NH3PbI3, catalogued in the Cambridge Structural Database (CSD). These include one CH3NH3PbI3•H2O10 and two (CH3NH3PbI3)2•H2O.12 The former and latter structures reported in 1987 and 2014 are having P21/n and P21/m space group symmetries, respectively. Figs. 1 a) & c) display the packed polyhedral, and two (CH3NH3PbI3)2•H2O crystal reported in 1987 and 2014. The later structure resembles one CH3NH3PbI3•H2O crystal reported in 2014,11 consisting of a distorted fcc array of the PbI6 octahedron, and the CH3NH3+ cations of two types and H2O molecules of a single type. Fig. 1 c) shows a 1x2x3 slab model for the hydrated structure reported by Wakamiya and coworkers,13 displaying the structural evolution of the unit cell, which has identical stoichiometry relative to the crystal reported in 1987,12 and that the H2O molecules in this crystal were introduced by exposing the sample to air. Nevertheless, as displayed in Fig. 1, both the crystals contain several PbI6 octahedra in higher dimension in which the each of the eight faces of a given octahedron can be realized.
equipped with an MA species, that is, \([\text{PbX}_n\text{MA}]^{m+}\). The attribute is not only reminiscent of the crystal of CH$_3$NH$_3$PbI$_3$, in the monoclinic phase, but also evident of its other known phases (vii. see abstract 3H03 for the pseudocubic phase).

While many possibilities exist, five conformers for each of the \([\text{PbX}_n\text{SnX}](\text{MA})_6^{m+}\) cations were optimized with DFT-PBE/Dzp, see Fig. 3a). The most stable of these in each set is found to be a structure of cation inversion symmetry, \(C_{1}\), \([\text{PbX}_n\text{SnX}](\text{MA})_6^{m+}\). The physical orientations of the CH$_3$NH$_3$ cations around the first coordination sphere of the \([\text{PbX}_n\text{SnX}]^{m+}\) anion in this stable cluster are similar to that of the (CH$_3$NH)$_3$PbI$_3$ crystal, CSD ref. code: FOLLIB. Its geometry is about 5.5, 24.7, 24.8, and 103.8 kcal mol$^{-1}$ relatively more stable than the four other high energy conformers identified (Fig. 3a). Of these latter four, the geometries of the intermediate two are first and second order saddle points, and the other two are genuine local minima. In all the high energy clusters, the eight organic cations facing the centers of the eight faces of the \([\text{PbX}_n\text{SnX}]^{m+}\) octahedron are perhaps significantly hydrogen bonded.

As already noted, the main focus of this investigation was to theoretically assess how, and to what extent, the \([\text{PbX}_n\text{SnX}](\text{MA})_6^{m+}\) coordination sphere can be affected by adding ten H$_2$O molecules among its surrounding, one at a time systematically in a stepwise manner. Since the DFT-PBE/DZP method (relative to many other DFT functionals and basis sets) produces the molecular HOMO-LUMO gap energy for the zero-dimensional CH$_3$NH$_3$PbI$_3$ cluster somehow closer to experimental band gaps reported for the higher dimensional analogues, the same method was utilized for the energy-minimization of the \([\text{PbX}_n\text{SnX}](\text{MA})_6^{m+}\) (\(N = \text{Cl}, \text{Br}, \text{I}\)) octahedron. Later, the H$_2$O molecules were added one by one to the outer second coordination spheres of each of the \([\text{PbX}_n\text{SnX}](\text{MA})_6^{m+}\) systems in a stepwise manner. The process was continued until all the \([\text{PbX}_n\text{SnX}](\text{MA})_6^{m+}\) cationic clusters were fully energy minimized.

While the knowledge of the positions of the H atoms in MA in the (CH$_3$NH)$_3$PbI$_3$H$_2$O crystal is completely lacking, the nature of hydrogen bonding interactions discussed in the literature is purely arbitrary. Fig. 2 depicts QTAIM molecular graphs for two selected clusters, the anhydrate \([\text{PbX}_n\text{SnX}](\text{MA})_6^{m+}\) and (the single water) hydrated \([\text{PbX}_n\text{SnX}](\text{H}_2\text{O})_6^{m+}\). It has greatly assisted us as identifying various kinds of such interactions, consistent with the recommended IUPAC signatures. For instance, the anhydrate cluster is stabilized by means of an extensive network of $\text{H}••\text{N}(\text{MA})$ and $\text{H}••\text{I}(\text{CMAS})$ intermolecular hydrogen bonded interactions, in which each MA involves in three of them. Such identifications are relied on the presence of the bond critical points (BCPs) of charge density between atomic basins, and the bond paths that connect them, and the short-to-long intermolecular distances for the above interactions (2.427–2.660 vs. 2.832–3.530 Å). The short $\text{H}••\text{I}–\text{N}$ distances explain the –NH part of MA is prone to reaction as is always observed tilted towards the face center, or the corner, or the edge of the octahedron in majorities of the halide perovskites crystals catalogued.

Upon an addition of a single H$_2$O molecule to the second coordination sphere of the \([\text{PbX}_n\text{SnX}](\text{MA})_6^{m+}\) ion, the geometry of the ion in the modified species is distorted, but it is not very significant that can degrade the closing-shell system completely, as having the sublimation of various species, e.g., NH$_3$, CCl$_3$, C$_2$H$_4$N, and H$_2$O, leaving the PbX$_n$ solid species alone.

A single H$_2$O molecule on the outer sphere of the \([\text{PbX}_n\text{SnX}](\text{MA})_6^{m+}\) cation produces an uncorrected binding energy $\Delta E$ of ~40.2 kcal mol$^{-1}$. Successive increase in the number of H$_2$O molecules around the cation increases the $\Delta E$ values for the hydrated cluster ions. The trend in increase in $\Delta E$ is non-additive cooperative. The most stable cation has ten H$_2$O molecules, \([\text{PbX}_n\text{SnX}](\text{H}_2\text{O})_{10}^{m+}\), with $\Delta E$ ~ 291.0 kcal mol$^{-1}$ (roughly ~29.1 kcal mol$^{-1}$ per H$_2$O). Fig. 3 shows a linear relationship between the number of the H$_2$O molecules \(n\) in the \([\text{PbX}_n\text{SnX}](\text{H}_2\text{O})_{n}^{m+}\) ion and the $\Delta E$. The graphs indicate that although the H$_2$O molecules distort the geometries of the \([\text{PbX}_n\text{SnX}](\text{MA})_6^{m+}\) ions, they increase the overall stabilities of the hydrated clusters at 0 or 298.15 K. At this range of temperatures, the perovskites might not degrade completely. The conclusion is also decisive regardless of the dimensionality of the halide perovskites.

The HOMO-LUMO gap is an important measure of the device quality of a material. Its value for \([\text{PbX}_n\text{SnX}](\text{MA})_6^{m+}\) in PBE/DZP calculated to be 3.07 eV. Addition of two H$_2$O molecules (first and second) around the coordination sphere of the ion has downshifted the gap to 2.65, and 2.62 eV, respectively. However, increasing this number to three (or, even up to ten) around the \([\text{PbX}_n\text{SnX}](\text{MA})_6^{m+}\) ion, the gap further increases in which the gap oscillates between 3.05 and 3.25 eV for all the cationic clusters investigated. For instance, the value of this gap was ca. 3.09, 3.13, 3.25 and 3.24 eV for \([\text{PbX}_n\text{SnX}](\text{H}_2\text{O})_{n}^{m+}\), respectively. This may mean the optical gap is almost unaffected by the presence of the H$_2$O molecules despite the significant geometrical distortions encountered. The conclusions drawn above for the \([\text{PbX}_n\text{SnX}](\text{MA})_6^{m+}\) hydrated systems can be applicable to the other hydrated clusters, viz., \([\text{PbX}_n\text{SnX}](\text{MA})_6^{m+}\) (\(N = \text{Cl}, \text{Br}, \text{I}\)) clusters.

[References]
3) S. Yakunin et al., Nat. Phys. 2015, 9, 444.