

Hybrid Organic–Inorganic Perovskites (HOIPs): Opportunities and Challenges

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1. Introduction

This article provides the collective, critical view of the authors, who convened at a workshop on hybrid organic–inorganic perovskites (HOIPs) in late February 2015, where challenges and opportunities for energy and optoelectronics research involving HOIP materials and devices were discussed. HOIP-based photovoltaic (PV) devices have made spectacular progress in terms of increased efficiency in the past few years. This rapid progress has created a situation where the technological advances measured by power-conversion efficiencies have proceeded much more quickly than the basic physics, chemistry, and materials science necessary to understand the materials and their composites from the perspective of synthesis, structure

and opto-electronic properties. The consensus from the workshop was that such an understanding is required if the true potential and limitations of this fascinating class of materials is to be fully realized. Such an understanding will aid the development of rational “design rules” leading to a variety of applications for HOIP-like materials. Herein, we highlight gaps in our collective understanding, we identify unique HOIP properties that have not (yet) been adequately explained (at the time of writing), and we suggest areas where additional fundamental, theoretical, synthetic, and processing studies as well as structure and property characterization, will facilitate building this understanding.

While HOIPs have been known for many decades,^[1,2] the modern study of these materials for optoelectronic devices

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Evolution of hybrid I-O Perovskite solar cells

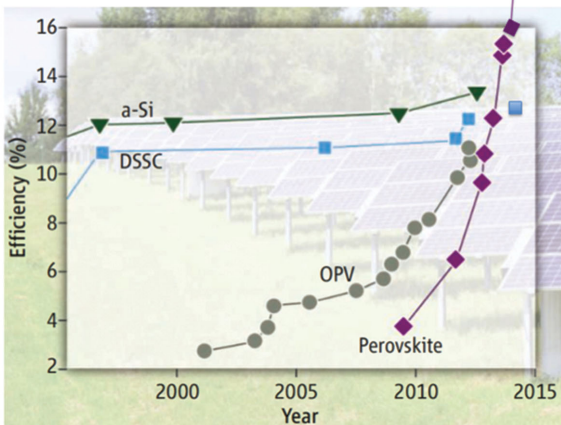


Figure 1. Illustration of the rapid increase in perovskite cell efficiencies. The increase achieved in the past four years is particularly notable. The cells have already achieved documented efficiencies >20%, which represents an unprecedented rate of progress compared to any other solar technology. Adapted from ref. [13], with updated HOIP data (labelled “perovskite” in figure). Adapted with permission.^[13] Copyright 2013, American Association for the Advancement of Science. OPV: organic photovoltaics; DSSC: dye-sensitized solar cell; a-Si: amorphous Si solar cell; Efficiency: solar to electrical power conversion efficiency of the best cells at the time.

was initiated in the 1990’s by Mitzi et al. at IBM.^[3–6] These studies demonstrated the spectacular versatility of this class of compounds to create new 2D functional materials. However, their exceptional utility for energy conversion applications only became apparent in the past several years, when significant photovoltaic conversion efficiencies were demonstrated. There has been recent rapid progress in the efficiency of HOIP PV devices, especially those based on methylammonium lead iodide (MAPbI₃), **Figure 1**. The rate of increase in efficiency (admittedly mostly on very small area cells—0.16 cm² is typical) is unprecedented in PV research and development. In terms of absolute efficiency, this has already brought this system into parity with the long established CdTe and CuInSe₂ thin film PV materials. In addition, these materials have already demonstrated potential for light emission,^[7–9] and may also provide other energy-related functionalities, such as in thermoelectrics.^[10] These functionalities appear to be based on the special composition-structure combination of HOIP materials, which yields superb carrier transport properties, likely owed in large part to their unusual energy band structure,^[11,12] see **Figure 2**.

The structure of the MAPbI₃ HOIP material has an octahedral coordination around the Pb atoms, and the methylammonium cations occupy the “interstices” (the A sites) within the ABX₃ perovskite lattice, which are sufficiently large to accommodate small organic cations (see **Figure 3**).

The unusual characteristics found to date raise many questions about the origin of the uniqueness of the HOIPs, such as structure(s), composition (e.g., combination of Pb and I or Br), electronic structure, and the presence and role of a

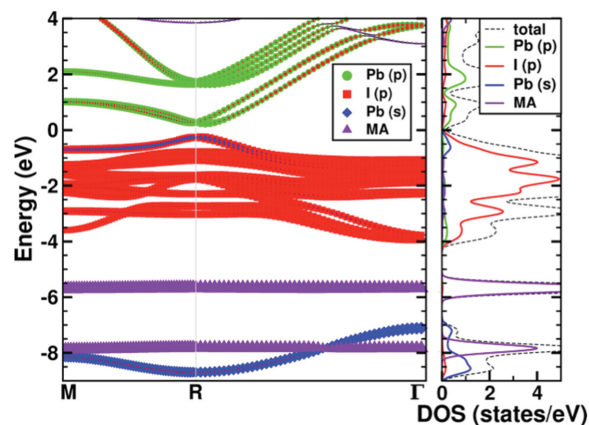


Figure 2. Band structure (left panel) and density of states (DOS, right panel) of MAPbI₃ in its cubic phase, calculated^[14] with density functional theory using the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation,^[15] including spin-orbit coupling (SOC). In the left panel, contributions of specific orbital character at each k-point are given by a color code: green circles depict Pb p, red squares I p, blue diamonds Pb s, and violet triangles MA states. M, R, and Γ correspond to (1/2, 1/2, 0), (1/2, 1/2, 1/2), and (0, 0, 0) k-points, respectively. In the right panel, projected DOS are shown using the same color coding as in the band structure. The VB largely consists of I 5p with some smaller contributions from Pb 6s states, whereas the CB is composed of Pb 6p with some contributions from I 5p orbitals. Note that while the PBE + SOC calculated band gap is smaller than the experimental one by ca. 1 eV,^[11] the assignment of the relevant bands is still in very good agreement with higher level GW calculations that include SOC.^[12]

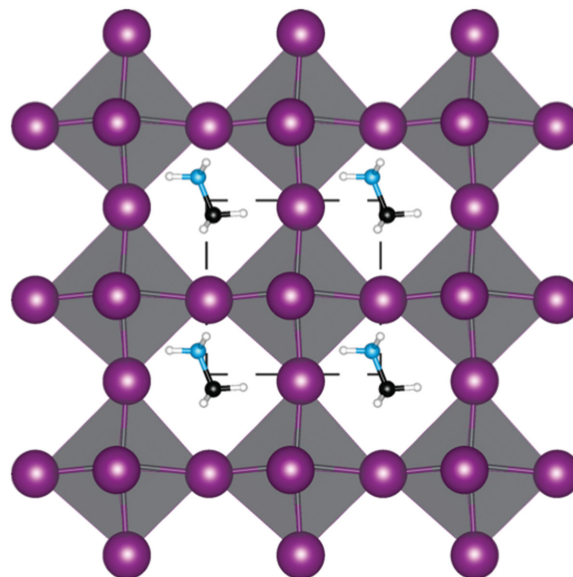


Figure 3. Schematic representation of methylammonium lead iodide (MAPbI₃).^[16] Dashed lines indicate the unit cell, containing carbon (black), nitrogen (blue), hydrogen (white), iodine (violet), and lead (light gray) atoms; note that the latter are inside the shaded octahedra. For convenient visualization, some atoms in adjacent unit-cells are shown. Although the MA⁺ cations appear ordered they are likely free to rotate and disordered.

large, organic cation (and possible expansion of the lattice). A more profound understanding of these characteristics should provide directions for identifying other materials that might have similarly remarkable properties, such as the possibility to be prepared under mild conditions; materials with high crystalline and electronic quality; and potential self-healing mechanisms during growth and possibly during excitation. Some key materials aspects to be considered are highlighted below.

2. Open Issues Regarding HOIPs

2.1. Uniqueness

The remarkable rise in interest in HOIPs for photovoltaics noted above, coupled with the ability to design, in principle, a range of similar compounds with different energy gaps by changing organic (e.g., methylammonium, MA; formamidinium, FA), metal (e.g., Pb, Sn) or halide (e.g., I, Cl, Br) constituents, generate key questions regarding the *uniqueness* of these materials, in particular with regards to their hybrid nature and the role of the organic cation. The initial success of these materials naturally motivates the search for design principles, which, if they can be found, could lead to a broader class of materials with many of the characteristics that are so attractive in HOIPs.

2.1.1. Unique Structural Aspects

In the perfect cubic HOIP structure, the organic cation occupies the cubo-octahedral cavity between corner-sharing octahedra (see Figure 3), in which it can rotate about its minimum energy position. This introduces a novel structural parameter, the importance of which is just beginning to be investigated.^[17] In particular, the ability of the cation to rotate^[18] could lead to dipole alignment under an external electric field, and have implications in terms of possible ferroic behavior for these materials.

2.2. Tell-Tale Electronic Properties?

2.2.1. Carrier Diffusion Lengths

The reported carrier diffusion lengths are remarkably large,^[19,20] and imply long carrier lifetimes, which have indeed been confirmed from optical experiments.^[19] The micrometer values (up to 100 μm), observed by several techniques, are similar to values seen in single crystal III-V semiconductors. Whether this can be attributed to the band structure of the material is unclear, as direct measurements of the band structure via angle-resolved photoemission spectroscopy (ARPES), are needed to complement these data and test the theoretical results.

Furthermore, whether these extremely long values^[19] represent true diffusion lengths is still a matter of debate. Another possibility is very long diffusion lengths in the material with (mostly) only one carrier, similar to what can be deduced

from experiments with single crystal electrodes in photoelectrochemical solar cells.^[21] To date, only single-crystal samples of very few direct band gap semiconductors are known to have comparable diffusion lengths. If they are true diffusion lengths, it is crucial to establish whether they result from extremely low defect densities (which would minimize scattering), low dark carrier densities (the ability to achieve close to intrinsic materials), small phonon-electron scattering cross sections, or possibly the speculated “ferroelectric domains”,^[22] which, however, requires clear evidence for ferroelectricity.

In parallel to evidence for long diffusion lengths, there have been reports of very low carrier effective masses (0.104 m_e).^[23] The importance of this point is readily understood by recalling that the mobility is inversely proportional to the effective mass of the charge carrier. The mobility, along with lifetime, defines the diffusion/drift length. It is therefore of fundamental interest to determine whether this is another special characteristic of these materials. How this can be measured on HOIP materials used today is still an unanswered question. The materials that show some of the more remarkable properties are nearly intrinsic (comparable hole and electron densities), making conventional Hall based transport measurements very difficult and more experimental Hall effect data are required to clarify this issue. While there are other approaches routinely used to evaluate the effective mass, such as ARPES, which can resolve the hole effective mass, these have not yet been reported for HOIPs. Finally, a critical step would be to correlate the electronic band structure to one or more of these factors.

2.3. Synthesis

Among HOIP characteristics, the exceptional electronic transport and low carrier recombination rates observed for solution-processed films rival those obtained with films fabricated via physical vapor deposition (PVD) and the best values achieved in only few other semiconductor systems, even as single crystals. This begs the question of how such high quality materials can be obtained by simple deposition techniques, such as spin-coating plus mild annealing and, in some cases, even in air.

However, despite early successes, there exists *tremendous variability in the quality of these films*, as evidenced by the structural heterogeneities observed by optical and electron microscopy. This variability points to the fact that the parameters that govern the formation of HOIP thin films, particularly the films that exhibit comparable optoelectronic properties to those found in traditional inorganic crystalline materials grown by far more equipment-intensive techniques, e.g., high temperature epitaxy, are not yet understood. Crystallinity and density of defects and impurities are in general determining factors for (opto)electronic properties, and are also highly dependent on the materials formation processes for most inorganic semiconductors. Understanding this behavior and the structure/property relationship is crucial to a fundamental understanding of HOIP materials and to an eventual extension of their properties to other process-tolerant systems.

From a materials synthesis point of view, it is also remarkable that the preparation (nucleation and growth) of HOIPs, both from solution and PVD, has been so successful.^[5,24] The fact that very few systems, in particular semiconductors, are produced with comparably high optical, electronic, and crystalline quality by both approaches must direct our attention to what is unique and can be learned from the synthesis pathways for these materials. As identical inorganic/organic hybrid frameworks form in both cases, the key to high quality materials apparently does not lie simply in the synthesis pathway, in particular with regards to species that lead to nucleation of the desired structures. Also unclear is the effect that organic and inorganic impurities have on the synthesis process (either beneficial or detrimental), as well as on optoelectronic properties of the material (see also next section). This is important as small amounts of impurities can have a favorable impact on the kinetics of nucleation and growth of other semiconductors prepared for PV.^[25,26]

A large part of the complexity lies in the fact that the chemical reaction for HOIP formation and its crystallization over macroscopic distances take place concurrently, and recent evidence suggests that precursors to the perovskite form as early as when the starting materials are co-dissolved in a common solvent.^[27] Dynamic light scattering and concurrently UV-vis spectroscopy measurements reveal the dynamic nature of the solution, with the emergence of sub-micron size particles and a simultaneous increase in absorbance in the ultra-violet range. Thus, efforts to decouple the chemical reactions from film formation and crystallization simplify the challenge and provide a handle for tackling their respective characterization. The thermodynamics for materials formation and the detailed temperatures used for the synthesis are not well documented. In a materials set where possibly nearly every species can diffuse, such knowledge is especially important. Given the optoelectronic performance of the methylammonium lead iodide to date, the material appears to be unique; however, not much is understood about how much substitution of the organic cation can be tolerated, or if there are combinations whereby inorganic ions, such as Cs⁺, can partially or entirely replace the organic cation, as has been shown for CsPbBr₃.^[28]

2.4. Materials Properties and their Independence/Dependence on Synthesis Approach

Historically it has been very difficult to produce comparable optoelectronic materials by PVD and solution-based approaches. HOIP materials seem to be a singular exception, where both approaches can produce similar high-performance materials—albeit with differences in grain structure and morphology—and subsequent devices with very comparable efficiencies and lifetimes. Several issues related to HOIP synthesis must be addressed to understand an apparent lack of dependence of materials properties on the synthesis approach (even though nominally identical methods can produce, even in a given laboratory, materials with a wide range of optoelectronic, and especially photovoltaic properties). A basic understanding of the nucleation and growth is essential for both solution and PVD approaches.^[29] The current view in

the field suggests that the formation of the active perovskite layer requires (at least some) annealing and proceeds via a sequence of crystallization stages, where a key stage is exfiltration of excess CH₃NH₃I (hypothesized as CH₃NH₂ and HI) salts during annealing, leading to the formation of a final HOIP phase. Still, formation of an initial “precursor” phase (that can be highly ordered) after deposition was noticed,^[29,30] while crystal nucleation leading to this phase occurs already in the deposition solution.^[31] Gaining a detailed insight into a complete crystallization path leading to an active layer will be important to advance the HOIP field.

The thermodynamics and kinetics for the HOIP growth are such that one apparently can grow hybrid perovskites with kinetics similar to those of grain growth. The often encountered problem of poor homogeneity of the product, which limits most high efficiency cells to small areas, may be alleviated by finding conditions that allow the optimization of the relative rates of grain growth and nucleation to obtain structural and compositional uniformity, while minimizing defects. Note that, in many cases, one must simultaneously form the correct phase, create nucleation sites and get grain growth, which if kinetics are appropriate, can generate large grains. If nucleation is slow and grain growth rapid, then one might expect that growth would be similar for vacuum and atmospheric growth. A related question is whether the growth is topotactic or, more generally, in some way templated by the substrate. For both vacuum and solution growth, as the reaction of precursors proceeds, it is important to identify what happens to excess reagents, solvents, or impurities, e.g., the HI stabilizer, generally H₃PO₂, heavy metal impurities in solvents or organic impurities. Crystal growth that either excludes impurities or is insensitive to them is quite remarkable (outside of small nanocrystals^[32]). Indeed, the effects of impurities on nucleation and growth of HOIPs are almost completely unknown. Similarities between materials prepared in different laboratories are therefore unclear, and metrics, i.e., experimental observables that enable a meaningful, *quantitative* comparison of materials, are essential to a baseline understanding of the growth processes.

2.4.1. Response to External Stimuli

Can the relatively low elastic modulus and nano-hardness of these materials (elastic modulus ≈14, slightly lower than some types of wood; and nano-hardness of 0.55 GPa, between wood and Au^[33]) explain their unique responses to external stimuli (electric field, illumination) due to the ease of polarization of one or more of its components, or possibly even the entire lattice (both Pb²⁺ and I⁻ are highly polarizable cations and anions, respectively)? What is known to date is that applying a voltage yields transport results (dark and light current-voltage characteristics) that suggest that the material can be poled with some poling retention time. Results from scanning piezo force microscopy seem to support this idea.^[34]

Whether the hysteresis observed in current-voltage characteristics, especially with oxide contacts, is an intrinsic property of the HOIP or is due to interfacial effects (pile-up of mobile ions at the ionically blocking electrodes has been suggested)

is not yet clear.^[35,36] Recent literature^[37] focuses on the structural changes arising from DC bias and illumination. There is increasing evidence that supra-band gap illumination can modify the materials beyond the presence of photo-generated electrons, holes, and excitons. It is possible that this behavior is due to the rotational degree of freedom of the organic cation, i.e., an electro- or photo-induced orientation of this cation.^[38] These ideas and interpretations can be clarified with in operando measurements (see also below).

To understand whether intrinsic and/or interfacial phenomena are important, it is critical to separate the effects of external stimuli on the bulk from those on the interfaces. To this end, it will be helpful to elucidate the effects of illumination, electric field, and temperature on bulk electronic, optical, structural, and device transport properties. In addition, due to the rather low elastic constants, measurements under pressure may well shed light on the importance of the “soft” nature of the materials. Such experiments may help shed light on potential ion migration and rotational or vibrational motion of the organic and other components (making a soft lattice more dense should inhibit such effects). Little is known about the stability of HOIP materials under pressure and the effect of pressure on them in general. Therefore, as a first experiment, it may be good to study whether PbX_2 can be transformed under pressure, possibly to a (defect) perovskite-like structure.

2.4.2. Ferroelectricity

As already noted above, it has been speculated that HOIP materials are ferroelectric^[22] and that this may have important consequences for their band structure and photovoltaic behavior. In particular, non-centrosymmetric materials can show a bulk photovoltaic effect,^[22,39–48] which can yield very high voltages at negligible currents. If present, domain walls between polar domains^[49–52] and interfaces between polar and nonpolar materials^[53] can separate carriers. To determine whether the material is ferroelectric (FE), it is necessary to measure the dielectric noise as a function of temperature and frequency and look for a FE signature. A more straightforward set of studies may be to seek evidence of pyroelectricity in HOIP single crystals, which is a less demanding property to characterize than ferroelectricity, but with relevance to possible poling effects.

2.5. Defects, Ion Migration and Materials Stability

2.5.1. Nature of Defects

Part of the answer to the question of what is unique and can be learned from these materials may lie in the nature of defects,^[54,55] and in the fact that these materials appear to exhibit remarkable tolerance for defects. Defects in optoelectronic materials (whether impurities or structural ones) often determine their properties and, above a certain density, deteriorate their performance and reduce the ability to control their properties. Usually very clean processing conditions and annealing (heating at elevated temperatures, and slow cooling)

of the product are used to decrease unwanted/uncontrolled defect densities. We use the concept of defect tolerance to indicate either a relative insensitivity of functional properties to defects, or a low density of defects in the material, even if no special measures are taken to avoid their formation during processing. The defect tolerance of HOIPs may be a result of their energy band structure, their hybrid organic-inorganic character, the relative ease of motion and redistribution of the ions, the possibility of phase separation into low defect phases in different proportion, and/or the polarizability of the constituent ions, to name a few possible reasons. Recent computational and experimental investigations have begun to focus on the issue of defects and electronic gap states; however, the nature and density of these bulk and surface defects, and the role of the organic cations, beyond insuring charge balance, are still mostly unknown. Yet, if HOIPs are truly defect-tolerant, the key challenge is whether we can deduce materials design principle(s) that will lead to other similarly tolerant systems.^[56]

2.5.2. Ion Migration

Directly related to the synthesis issues is the relative importance of ionic migration in growth. But subsequent materials stability is just as important. Ionic migration may also play a key role in the current-voltage (I–V) hysteresis behavior often observed in photovoltaic cells comprising these materials, as hysteresis was shown to be a characteristic for mixed ionic electronic conductor (MIEC) materials.^[57] This is very important, as ionic migration, an intrinsic property, cannot be averted by encapsulation. Migration can be complex if constituent species and impurities are potentially mobile at room temperature in these materials. The room temperature migration of large cations or anions, such as the CH_3NH_3^+ , Γ^- and Pb^{2+} constituents in MAPbI_3 (but see below regarding possible proton motion), would present a major shift in thinking about solid state *inorganic* materials chemistry (it is known from work on organic molecular and polymer semiconductors that dopants with relatively large molecular volume can migrate,^[58] but the interactions between the constituent species in an organic solid are normally orders of magnitude weaker than in the bonded inorganic solid).

A number of reports have appeared on MAPbI_3 with data that are interpreted to show ion migration,^[34,59,60] in one case of iodide,^[59] in another case of methylammonium.^[60] In view of the ease of decomposition of MAPbI_3 into its binary components (based on the mild conditions needed for its two-step preparation from PbI_2 exposure to CH_3NH_3 ^[61]) and the low decomposition potential for $\text{CH}_3\text{NH}_3\text{I}$, the possibility of decomposition instead of, or in addition to, migration needs to be checked thoroughly. Specifically, these experiments must be able to separate decomposition from ion migration. While this does not mean that ion migration does not take place (as it may be connected with the “soft” character of these hybrid materials mentioned above), more in-depth experimental investigations are needed to find conclusive evidence for the occurrence of ion migration and for which ions migrate, in a manner customarily used in the field of solid-state ionics. If validated,

then the migration process may provide a way to reconcile seemingly contradictory properties, e.g., it may be the basis for the suggested defect tolerance/self-healing. In addition, H⁺ migration, which is easy to imagine for HOIPs, could alter our basic understanding of the materials, in general.^[62] A hopping mechanism for protons or other impurities, possibly akin to the Grotthuss mechanism, which results in high ion mobility and low activation energy, is a possibility.^[62] It is important to understand, for a particular ion, whether its motion is intrinsic or depends on defects, what is the real activation energy for diffusion, and how grain boundaries and defects affect the rate and activation energy. If protons are moving, their source, e.g., organic cation, water, or other sites must be elucidated.

On a more general note, it will be helpful to realize that the behavior that is emerging for the HOIP materials, in terms of co-existence of ionic and electronic conduction, is not unique in solid-state materials. Indeed, CuInSe₂ and its alloys are well-known MIEC photovoltaic materials in which Cu⁺ can migrate, a property that imparts self-healing characteristics to these compounds.^[63–65] In another class of devices, the light-emitting electrochemical cells, LECs,^[66,67] already associated with the HOIP PV behavior recently,^[68] MIEC behavior is a *sine qua non*. A didactic review on MIECs can be found in ref.^[69]

2.5.3. Materials Stability

There are many aspects of material stability, including extrinsic stability to external contaminants and intrinsic instability to potential chemical reactions, phase transformations, and/or ion/atom diffusion that can occur in the materials. To understand potential instabilities, there needs to be active evaluation of the materials stability *in situ* and *in operando*, and of different reaction paths as a function of external conditions, namely temperature, ambient atmosphere, and reactions at interfaces. Therefore, it is necessary to evaluate the key thermodynamic properties. To date, little or no detailed analysis by thermal gravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) has been reported.^[70,71] The results, together with associated synthesis observations, suggest that ΔG_{form} is low for HOIPs, perhaps as low as 0.1 eV, as suggested by computational results.^[72] If true, this would be very significant, as it implies high defect densities, structural disorder and coexisting materials phases. Interestingly, it appears that the HOIP materials either have none or are insensitive to these characteristics, as implied by, for example, the (very) long carrier diffusion lengths/lifetimes (few defects) and the high crystallinity (structural order). While the low formation energy is consistent with the facile decomposition of methylammonium iodide from the perovskite at even relatively low temperatures, the presence of small amounts of lead iodide does not appear to significantly hinder the PV properties. These characteristics seem to support a defect tolerance, which can eliminate defects as they form (self-healing), or to point to an insensitivity of the fundamental PV characteristics to the existence of secondary phases.

Materials stability and defect tolerance may also be related to details in cohesion and related mechanical properties of these materials. The very different elements that constitute HOIPs

in principle allow for a multitude of interactions that include covalent and ionic contributions, but also “weaker” interactions such as van der Waals (vdW) and hydrogen bonding. The notion of a more complex form of crystal cohesion in HOIPs has been put forward early on,^[5] and was more recently substantiated using dispersion-corrected density functional theory calculations.^[73] In particular, the role of vdW as well as hydrogen-bonding interactions between the organic and inorganic parts of HOIPs has been highlighted.^[74] Similar to metal–organic framework materials,^[75] cohesion in HOIPs thus seems to be more complex.

Regarding the overall response of HOIPs to mechanical perturbation, the compressibility via the bulk modulus of Sn–I based HOIPs containing MA and FA cations has been measured.^[76] While the MA-based species yielded a bulk modulus of 13 GPa, FASnI₃ was found to be significantly more compressible.^[76] This was ascribed to the lower overall structural stability of FASnI₃ due to the rather large size of FA.^[76] More recently, Feng used dispersion-corrected density functional theory to compute the elastic properties of HOIPs.^[77] As an example, the Young's modulus of MAPbI₃ was found to be between 13 and 22 GPa, depending on the phase considered in the calculations.^[77] The Poisson ratio, which gives the relation between axial and transverse distortions, was calculated to be ca. 0.3.^[77] Compared to other perovskites and inorganic semiconductors, Young's modulus of MAPbX₃ is smaller by several tens of GPa. Therefore, HOIPs seem to be much “softer” than traditional inorganic semiconductors, but they are still much stiffer than conventional soft materials.

3. Alternative Material Compositions

As noted above, there is considerable current discussion regarding the “uniqueness” of materials that contain both Pb²⁺ and I[−] or Br[−], as MAPbI₃, and more recently also MAPbBr₃ have shown excellent PV performance, superior to those of other HOIPs. Sn-based systems are similar to Pb-based ones with respect to structure and growth, but not in terms of PV performance. Likewise, there is only one report at present of a PV cell based on all-inorganic perovskite with performance approaching that of its HOIP analogue.^[28] Systematic comparisons of these systems (with and without organic cation) employing the Pb- and I- or Br-containing candidates, both in terms of basic structural, optical, electronic, dielectric and elastic properties, will provide a broader view of the landscape of structures and properties of the materials that do contain an organic moiety, i.e., the HOIPs. These explorations are necessary for gaining the necessary insight to understand what is unique about, and how to identify new HOIP-like materials. As the basic understanding of the origin(s) of the key HOIP properties becomes established, design rules and new compositions with enhanced performance will evolve.

We further note that HOIPs cover a wide range of band gap energies, spanning more than 2 eV from MASnI₃ (1.1 eV) to MAPbI₃ (1.6 eV), MAPbBr₃ (2.3 eV) and MAPbCl₃ (≈3.1 eV), and presumably adjustable, to some extent, in-between with mixed metal and/or halide compounds, such as MAPbI_xBr_{3−x} or MAPb_{1−y}Sn_yX₃.^[1,2,5,78–81] Further small adjustments are

also possible by replacing some, or all, of the organic cations, e.g., MA⁺ by formamidinium.^[82–86] This range of band gap energies is compatible with multiple applications in (opto) electronic devices beyond photovoltaics, despite the overwhelming focus on the latter in the research activities of the past four years.

4. Important Questions for Design Principles and Approaches to Address Them

The remarks outlined above lead to a set of key questions that must be addressed in order to increase our understanding of the fundamental properties of hybrid perovskites and, ultimately, inform on the design and synthesis of new, high-performing HOIP-like materials.

- Is the band structure a unique signature for defect tolerance?
- Is a lone electron pair on the metal cation critical?
- Is the metal coordination number of 6, instead of the usual 4 for conventional semiconductors, critical?
- Is the presence of multivalent cations in their low (reduced) valence state important?
- Can other metal–anion structure types produce structures as tolerant of defects as MAPbI₃ seems to be?
- Can 2D structures (achievable using larger organic cations) be informative models?

Based on the outcome of the workshop and the extensive knowledge gaps outlined above, the workshop participants created an experimental and a theoretical/computational matrix of potential approaches that should rapidly provide a better understanding of HOIP materials. These approaches are discussed below. We trust that this understanding will lead to answers for many outstanding questions and will guide the discovery of similar materials, ultimately resulting in better and more reliable HOIP-based devices. Here we focus on some of the key observations.

4.1. Experimental Characterization

We distinguish three areas of characterization: 1) the materials themselves, 2) contacts and interfaces, and 3) device structures.

4.1.1. Materials Characterization (Composition and Structure)

Surprisingly little basic characterization has been reported for the materials needed to make MAPbI₃ and, where some has been done, it has not been done universally on very high quality materials. As single crystals become available, more of these basic studies are warranted and differences between single crystals and polycrystalline films can be subjected to experimental scrutiny. Knowledge of the actual chemical composition and deviations from stoichiometry will be of prime importance to understand the materials electronic properties. As noted above, a key type of characterization is that of basic thermal analyses, especially to look at low temperature transitions and volatile

species. This should also help support emerging computational efforts to understand how a defect tolerant materials system can form. Using electron microscopy (EM), X-ray diffraction (XRD), secondary ion mass spectrometry (SIMS) and Raman spectroscopy should help delineate the surface chemistry and define the composition and structure as a function of depth. Tracking the structural evolution with in situ characterization techniques will provide an opportunity to quantify crystallization/phase transformation kinetics, possibly shedding light on the mechanism by which these transformations take place. It is especially important to understand the structure at the bottom perovskite-on-substrate interface, as it defines the subsequent growth of the HOIP film. These studies may also begin to elucidate the nature of the defects in the materials, substantiating the relationship between non-trapping and non-scattering with theory. Other key measurements include ionic diffusivity of the various species as a function of temperature and applied bias. It is important to understand the local movement, for example of the organic cation as well as the potential diffusion of the halide. Ideally, these should be monitored in-situ by techniques like Fourier transform infra-red (FTIR) spectroscopy, Rutherford backscattering (RBS), or by use of isotopes. Detailed photoluminescence may be able to support these measurements. Related to this is a direct measurement of the mechanical and thermal properties of the materials and their resultant elastic constants and coefficients of thermal expansion, which are directly related to their growth and stability. In light of the recent computational results on mechanical properties mentioned above,^[77] it will be interesting to also establish experimentally how the mechanical properties of HOIPs relate to those of other materials, such as molecular crystals. These studies should provide insight into one of the most vexing questions for these materials, that of their basic stability. It is known that they are extrinsically unstable and can potentially react with water and/or oxygen. However, in the absence of these external factors, it is unclear whether they can be intrinsically stable within a certain range of environmental parameters such as temperature and illumination.

4.1.2. Contacts/Interfaces

There are very few experimental data on the electronic structure and surface chemistry of these interfaces. Given their potentially “soft” nature and their dynamic character, it is not clear how properties such as the work function, surface chemistry and surface defect structure change with processing and external effects like temperature and illumination, both because of the sample preparation restrictions (so as not to alter the material) and light, electron or ion beam-induced damage during measurement. Detailed microscopic non-contact atomic force microscopy (AFM)- and scanning tunneling microscopy (STM)-based approaches should provide important information on this. Can we find evidence for surface ionic migration, its dependence on illumination, and whether it involves higher or lower activation energies than in the bulk? Impedance spectroscopy may be of use, ideally under illumination, but such experiments present serious challenges in terms of interpretation of the results. Use of relatively large single crystals should be

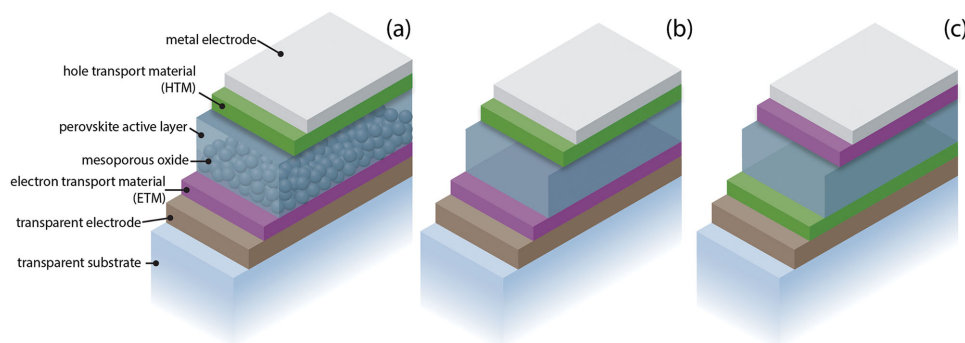


Figure 4. Schematic representation of different HOIP-PV device architectures with the a) mesoporous, b) planar, and c) planar-inverted device stacks. Extensive work within the community has clearly demonstrated some ambiguity as to the optimum device stack configuration.

useful in these studies, as will the growth of HOIP on lattice-matched substrates.

4.1.3. Device Characterization

An important question regarding HOIPs is how much lateral uniformity exists across a grain or grains. While significant progress has been made in the past year in making larger area ($>1 \text{ cm}^2$) cells with efficiencies above 10%, and a 95 cm^2 module with 9% efficiency was recently reported,^[87] most reported studies still use $0.1\text{--}0.2 \text{ cm}^2$ cells. In addition, equivalent efficiencies have been reported across the different device architectures shown in **Figure 4**, with no clear insight into the underlying device physics. At the same time, carrier diffusion lengths on the order of hundreds of microns or millimeters were reported.^[19] This lack of insight into the operational principles of the device and uncertainty on how to scale the devices appropriately calls for mapping the optoelectronic/device properties as a function of lateral position. Techniques such as light/electron beam-induced current (LBIC/EBIC) will be very useful in this respect, although care must be taken to avoid beam damage, especially with the latter. Also, measuring the true transport properties as a function of both position and temperature should give some insight into the Hall coefficient and the actual mobility and carrier concentration. Hysteresis has been reported to be present or absent, depending on sample and details of materials choices with respect to the contacts. While some correlation with grain size or type of interface (with oxide or organic phase) has been noted, the true nature of this effect remains unknown.^[35,68,88,89] Given the potential impact of ionic diffusion on device properties, this could be a factor in defining where hysteresis occurs. This relates directly to the materials properties mentioned above, as well as the nature and stability of the interface. As such, it is crucial to look at the illuminated and dark device properties across a wide range of time scales, from those of ion motion to that of bias-dependent diffusion.

4.2. Theory, Modeling, and Computational Studies

Related to the categories above, but slightly more global, is the need for more computational work for these materials,

specifically in the areas of process space, structure-composition space, and band structure-transport space.

4.2.1. Modeling Process Space

At present, very little is known about the larger family of HOIP perovskites. In particular it is important to understand the nucleation and growth energetics and mechanisms to try and understand the differences to be anticipated as a function of synthesis pathway. This would include the ΔG and ΔH of the reactants and products and potential impurity phases. One also must take into account the ionic diffusion pathways as a function of temperature. How very high coordination numbers and lone electron pair and the relative soft/hard characteristics of the ions affect these models is unknown. Molecular dynamics can help with the large assemblies encountered. Lead dihalides may be good reference materials to study.

4.2.2. Structure–Composition Space

This area looks both at the details for the current structure, for example modeling how much room there is available in the HOIP structure and what ions can be accommodated. This includes the search for structures, analog ones or others, which may have characteristics similar to those of HOIPs. Such understanding may lead to the development of a more complete set of design rules that could help guide chemical synthesis and experimental efforts in the field. Directly related to these calculations are those that would map the defect structures in both the films and at the interfaces, and elucidate the electronic nature of those defects. Local structural transformations can also potentially be mapped and this will feed back to the general synthesis modeling above.

4.2.3. Band Structure–Transport Space

There is much speculation that, in HOIP materials, a defect-tolerant band structure is a key element that defines the uniqueness of the materials, especially for solar applications. Interestingly, in the inorganic PV realm,^[90] this same sort of

thinking is becoming central to new materials discovery. Here the HOIP materials have a number of unique properties that call for improved computational approaches. These include improvements in calculating band gaps^[11,12] and the effective masses for these materials, the latter to ascertain if the reported low effective masses can be modeled. Improvements in computations are also needed to investigate the origin and general applicability of the apparent defect-tolerant band structure, and whether this points to fully inorganic analogues or not. Finally, there is considerable controversy in the literature^[38,47,91] about the importance of the dielectric behavior of the materials in terms of the orientation of the organic cations in the structure and of ferroelectric (and related properties, e.g., piezoelectric) behavior. If the existence of any of these properties can be established, issues remain as to the extent to which these affect the subsequent optoelectronic device behavior either as a PV material or for light emission.

5. Opportunities and Conclusions

Throughout this essay, we attempted to put forward a number of fundamental issues concerning HOIP semiconductors, which to date remain either unexplored or unresolved in the literature. It is likely that research on, and eventually resolution of, these issues can greatly enhance the development and reliability of known HOIP materials and the discovery of novel, HOIP-like-materials. However, one of the most vexing issues in a field currently dominated by a race toward ever-improved PV device efficiencies is the lack of reproducibility of materials quality, from laboratory to laboratory, from preparation method to preparation method, from run to run, and from device to device. Establishing solid common grounds between materials researchers, working on and with materials appears therefore as a sine qua non condition for making real progress toward understanding, and eventually controlling, the properties of these materials. One of the main conclusions of the workshop is therefore a call for various steps to be taken to establish such a common ground.

- Establish confidence among experimental research groups
 - Develop sample transfer protocols to allow samples from one group to be transferred to another for measurement and study.
 - Develop standard measurements; share samples to verify measurements on same materials and devices.
 - Establish clear and sufficient standards for reporting sample preparation conditions; treat such documents as a living document for reporting in venues such as *Inorganic Synthesis*
- Focus on measuring heterogeneity
 - Examine sample-to-sample compositional and morphological variability, as function of synthesis route
 - Examine the same issues within a single sample, on multiple length scales
 - Key question: What is the minimum set of commonly available characterization techniques to define sample structural, compositional, and optoelectronic heterogeneity?
- Focus on elucidating fundamental material properties
 - To constrain simulations: obtain reliable values (multiple groups and wherever possible also multiple types of

measurements) of formation energy, elastic moduli, dielectric constants.

- To constrain experiments: measure what is critical radiation, electron and ion beam damage (and if it depends on material preparation) and decomposition routes under various atmospheric conditions

We argue that many of the interesting basic science questions identified and outlined in this article, along with preliminary suggestions for approaches that may yield suitable answers, will be resolved if these systematic investigations are developed. We are optimistic that progress in the basic science of these fascinating materials will greatly assist their technological development as well.

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- [1] D. Weber, *Z. Für Naturforschung B* **1978**, *33*, 1443.
- [2] A. Poglitsch, D. Weber, *J. Chem. Phys.* **1987**, *87*, 6373.
- [3] D. B. Mitzi, C. A. Feild, W. T. A. Harrison, A. M. Guloy, *Nature* **1994**, *369*, 467.
- [4] D. B. Mitzi, S. Wang, C. A. Feild, C. A. Chess, A. M. Guloy, *Science* **1995**, *267*, 1473.
- [5] D. B. Mitzi, in *Progress in Inorganic Chemistry*. (Ed: K. D. Karlin), John Wiley & Sons, Inc., Hoboken, NJ, USA, **1999**, pp. 1–121.
- [6] D. B. Mitzi, K. Chondroudis, C. R. Kagan, *IBM J. Res. Dev.* **2001**, *45*, 29.
- [7] K. Chondroudis, D. B. Mitzi, *Chem. Mater.* **1999**, *11*, 3028.
- [8] I. Koutselas, P. Bampoulis, E. Maratou, T. Evagelinou, G. Pagona, G. C. Papavassiliou, *J. Phys. Chem. C* **2011**, *115*, 8475.
- [9] Z.-K. Tan, R. S. Moghaddam, M. L. Lai, P. Docampo, R. Higler, F. Deschler, M. Price, A. Sadhanala, L. M. Pazos, D. Credgington, F. Hanusch, T. Bein, H. J. Snaith, R. H. Friend, *Nat. Nanotechnol.* **2014**, *9*, 687.
- [10] Y. He, G. Galli, *Chem. Mater.* **2014**, *26*, 5394.
- [11] J. Even, L. Pedesseau, J.-M. Jancu, C. Katan, *J. Phys. Chem. Lett.* **2013**, *4*, 2999.
- [12] F. Brivio, K. T. Butler, A. Walsh, M. van Schilfgaarde, *Phys. Rev. B* **2014**, *89*, 155204.
- [13] G. Hodes, *Science* **2013**, *342*, 317.
- [14] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169.
- [15] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
- [16] K. Momma, F. Izumi, *J. Appl. Crystallogr.* **2008**, *41*, 653.
- [17] C. Motta, F. El-Mellouhi, S. Kais, N. Tabet, F. Alharbi, S. Sanvito, *Nat. Commun.* **2015**, *6*, 7026.
- [18] O. Knop, R. E. Wasylshen, M. A. White, T. S. Cameron, M. J. M. V. Oort, *Can. J. Chem.* **1990**, *68*, 412.

- [19] Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao, J. Huang, *Science* **2015**, *347*, 967.
- [20] D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y. Losovyj, X. Zhang, P. A. Dowben, O. F. Mohammed, E. H. Sargent, O. M. Bakr, *Science* **2015**, *347*, 519.
- [21] G. Hodes, P. V. Kamat, unpublished.
- [22] J. M. Frost, K. T. Butler, F. Brivio, C. H. Hendon, M. van Schilfgaarde, A. Walsh, *Nano Lett.* **2014**, *14*, 2584.
- [23] A. Miyata, A. Mitioglu, P. Plochocka, O. Portugall, J. T.-W. Wang, S. D. Stranks, H. J. Snaith, R. J. Nicholas, arXiv:1504.07025 **2015**.
- [24] S. D. Stranks, P. K. Nayak, W. Zhang, T. Stergiopoulos, H. J. Snaith, *Angew. Chem. Int. Ed.* **2015**, *54*, 3240.
- [25] A. Rockett, *Thin Solid Films* **2005**, *480–481*, 2.
- [26] M. Yuan, D. B. Mitzi, W. Liu, A. J. Kellock, S. J. Chey, V. R. Deline, *Chem. Mater.* **2010**, *22*, 285.
- [27] K. G. Stamplecoskie, J. S. Manser, P. V. Kamat, *Energy Env. Sci* **2015**, *8*, 208.
- [28] M. Kulbak, D. Cahen, G. Hodes, *J. Phys. Chem. Lett.* **2015**, *6*, 2452.
- [29] D. T. Moore, H. Sai, K. W. Tan, D.-M. Smilgies, W. Zhang, H. J. Snaith, U. Wiesner, L. A. Estroff, *J. Am. Chem. Soc.* **2015**, *137*, 2350.
- [30] W. Zhang, M. Saliba, D. T. Moore, S. K. Pathak, M. T. Hörantner, T. Stergiopoulos, S. D. Stranks, G. E. Eperon, J. A. Alexander-Webber, A. Abate, A. Sadhanala, S. Yao, Y. Chen, R. H. Friend, L. A. Estroff, U. Wiesner, H. J. Snaith, *Nat. Commun.* **2015**, *6*, 6142.
- [31] Y. Tidhar, E. Edri, H. Weissman, D. Zohar, G. Hodes, D. Cahen, B. Rybtchinski, S. Kirmayer, *J. Am. Chem. Soc.* **2014**, *136*, 13249.
- [32] K. P. Johansson, G. McLendon, A. P. Marchetti, *Chem. Phys. Lett.* **1991**, *179*, 321.
- [33] S. Cohen, Y. Rakita, G. Hodes, D. Cahen, unpublished.
- [34] Z. Xiao, Y. Yuan, Y. Shao, Q. Wang, Q. Dong, C. Bi, P. Sharma, A. Gruverman, J. Huang, *Nat. Mater.* **2014**, *14*, 193.
- [35] W. Tress, N. Marinova, T. Moehl, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel, *Energy Env. Sci* **2015**, *8*, 995.
- [36] Y. Zhang, M. Liu, G. E. Eperon, T. C. Leijtens, D. McMeekin, M. Saliba, W. Zhang, M. de Bastiani, A. Petrozza, L. M. Herz, M. B. Johnston, H. Lin, H. J. Snaith, *Mater Horiz* **2015**, *2*, 315.
- [37] R. Gottesman, E. Haltzi, L. Gouda, S. Tirosh, Y. Bouhadana, A. Zaban, E. Mosconi, F. De Angelis, *J. Phys. Chem. Lett.* **2014**, *6*, 2662.
- [38] E. J. Juarez-Perez, R. S. Sanchez, L. Badia, G. Garcia-Belmonte, Y. S. Kang, I. Mora-Sero, J. Bisquert, *J. Phys. Chem. Lett.* **2014**, *5*, 2390.
- [39] V. M. Fridkin, A. A. Grekov, A. I. Rodin, E. A. Savchenko, T. R. Volk, *Ferroelectrics* **1973**, *6*, 71.
- [40] T. Choi, S. Lee, Y. J. Choi, V. Kiryukhin, S.-W. Cheong, *Science* **2009**, *324*, 63.
- [41] S. M. Young, A. M. Rappe, *Phys. Rev. Lett.* **2012**, *109*, 116601.
- [42] I. Grinberg, D. V. West, M. Torres, G. Gou, D. M. Stein, L. Wu, G. Chen, E. M. Gallo, A. R. Akbashev, P. K. Davies, J. E. Spanier, A. M. Rappe, *Nature* **2013**, *503*, 509.
- [43] Y. Kutes, L. Ye, Y. Zhou, S. Pang, B. D. Huey, N. P. Padture, *J. Phys. Chem. Lett.* **2014**, *5*, 3335.
- [44] J. Wei, Y. Zhao, H. Li, G. Li, J. Pan, D. Xu, Q. Zhao, D. Yu, *J. Phys. Chem. Lett.* **2014**, *5*, 3937.
- [45] J. M. Frost, K. T. Butler, A. Walsh, *APL Mater.* **2014**, *2*, 081506.
- [46] B. Chen, J. Shi, X. Zheng, Y. Zhou, K. Zhu, S. Priya, *J. Mater. Chem. A* **2015**, *3*, 7699.
- [47] Z. Fan, J. Xiao, K. Sun, L. Chen, Y. Hu, J. Ouyang, K. P. Ong, K. Zeng, J. Wang, *J. Phys. Chem. Lett.* **2015**, *6*, 1155.
- [48] F. Zheng, H. Takenaka, F. Wang, N. Z. Koocher, A. M. Rappe, *J. Phys. Chem. Lett.* **2015**, *6*, 31.
- [49] V. M. Fridkin, I. M. Gorelov, A. A. Grekov, V. A. Lyakhovitskaya, A. I. Rodin, *Sov. Phys. JETP Lett* **1966**, *4*, 310.
- [50] S. Y. Yang, J. Seidel, S. J. Byrnes, P. Shafer, C.-H. Yang, M. D. Rossell, P. Yu, Y.-H. Chu, J. F. Scott, J. W. Ager, L. W. Martin, R. Ramesh, *Nat. Nanotechnol.* **2010**, *5*, 143.
- [51] S. M. Young, F. Zheng, A. M. Rappe, *Phys. Rev. Lett.* **2012**, *109*, 236601.
- [52] S. Liu, F. Zheng, N. Z. Koocher, H. Takenaka, F. Wang, A. M. Rappe, *J. Phys. Chem. Lett.* **2015**, *6*, 693.
- [53] V. M. Fridkin, K. Kreher, *Phys. Status Solidi A* **1970**, *2*, 281.
- [54] W.-J. Yin, T. Shi, Y. Yan, *Appl. Phys. Lett.* **2014**, *104*, 063903.
- [55] W.-J. Yin, T. Shi, Y. Yan, *Adv. Mater.* **2014**, *26*, 4653.
- [56] R. E. Brandt, V. Stevanovi, D. S. Ginley, T. Buonassisi, *MRS Commun.* **2015**, *5*, 265.
- [57] D. Kalaei, I. Riess, *Solid State Ion.* **2014**, *262*, 883.
- [58] A. Dai, A. Wan, C. Magee, Y. Zhang, S. Barlow, S. R. Marder, A. Kahn, *Org. Electron.* **2015**, *23*, 151.
- [59] T.-Y. Yang, G. Gregori, N. Pellet, M. Grätzel, J. Maier, *Angew. Chem.* **2015**, *127*, 8016.
- [60] Y. Yuan, J. Chae, Y. Shao, Q. Wang, Z. Xiao, A. Centrone, J. Huang, *Adv. Energy Mater.* **2015**, DOI: 10.1002/aeem.201500615.
- [61] J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, M. Grätzel, *Nature* **2013**, *499*, 316.
- [62] D. A. Egger, L. Kronik, A. M. Rappe, *Angew. Chem. Int. Ed.* **2015**, DOI: 10.1002/anie.201502544.
- [63] D. Cahen, L. Chernyak, *Adv. Mater.* **1997**, *9*, 861.
- [64] J.-F. Guillemoles, U. Rau, L. Kronik, H.-W. Schock, D. Cahen, *Adv. Mater.* **1999**, *11*, 957.
- [65] I. Lubomirsky, D. Cahen, *Solid State Ion.* **2000**, *136–137*, 559.
- [66] Y. Cao, G. Yu, A. J. Heeger, C. Y. Yang, *Appl. Phys. Lett.* **1996**, *68*, 3218.
- [67] S. B. Meier, D. Tordera, A. Pertegás, C. Roldán-Carmona, E. Ortí, H. J. Bolink, *Mater. Today* **2014**, *17*, 217.
- [68] D. A. Egger, E. Edri, D. Cahen, G. Hodes, *J. Phys. Chem. Lett.* **2015**, *6*, 279.
- [69] I. Riess, in *CRC Handbook of Solid State Electrochemistry* (Eds: P. J. Gellings, H. J. M. Bouwmeester), CRC Press, Boca Raton, FL, USA, **1997**, pp. 223–268.
- [70] A. E. Williams, P. J. Holliman, M. J. Carnie, M. L. Davies, D. A. Worsley, T. M. Watson, *J. Mater. Chem. A* **2014**, *2*, 19338.
- [71] A. Dualeh, P. Gao, S. I. Seok, M. K. Nazeeruddin, M. Grätzel, *Chem. Mater.* **2014**, *26*, 6160.
- [72] A. Buin, P. Pietsch, J. Xu, O. Voznyy, A. H. Ip, R. Comin, E. H. Sargent, *Nano Lett.* **2014**, *14*, 6281.
- [73] Y. Wang, T. Gould, J. F. Dobson, H. Zhang, H. Yang, X. Yao, H. Zhao, *Phys. Chem. Chem. Phys.* **2014**, *16*, 1424.
- [74] D. A. Egger, L. Kronik, *J. Phys. Chem. Lett.* **2014**, *5*, 2728.
- [75] J. C. Tan, A. K. Cheetham, *Chem. Soc. Rev.* **2011**, *40*, 1059.
- [76] Y. Lee, D. B. Mitzi, P. W. Barnes, T. Vogt, *Phys. Rev. B* **2003**, *68*, 020103R.
- [77] J. Feng, *APL Mater.* **2014**, *2*, 081801.
- [78] S. A. Kulkarni, T. Baikie, P. P. Boix, N. Yantara, N. Mathews, S. Mhaisalkar, *J. Mater. Chem. A* **2014**, *2*, 9221.
- [79] F. Hao, C. C. Stoumpos, R. P. H. Chang, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2014**, *136*, 8094.
- [80] Y. Ogomi, A. Morita, S. Tsukamoto, T. Saitho, N. Fujikawa, Q. Shen, T. Toyoda, K. Yoshino, S. S. Pandey, T. Ma, S. Hayase, *J. Phys. Chem. Lett.* **2014**, *5*, 1004.
- [81] E. Mosconi, P. Umari, F. De Angelis, *J. Mater. Chem. A* **2015**, *3*, 9208.
- [82] D. B. Mitzi, K. Liang, *J. Solid State Chem.* **1997**, *134*, 376.
- [83] N. Pellet, P. Gao, G. Gregori, T.-Y. Yang, M. K. Nazeeruddin, J. Maier, M. Grätzel, *Angew. Chem. Int. Ed.* **2014**, *53*, 3151.
- [84] A. Amat, E. Mosconi, E. Ronca, C. Quarti, P. Umari, M. K. Nazeeruddin, M. Grätzel, F. De Angelis, *Nano Lett.* **2014**, *14*, 3608.

- [85] N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo, S. I. Seok, *Nature* **2015**, *517*, 476.
- [86] A. Binek, F. C. Hanusch, P. Docampo, T. Bein, *J. Phys. Chem. Lett.* **2015**, *6*, 1249.
- [87] F. Matteocci, L. Cina, F. Di Giacomo, S. Razz, S. Casaluci, A. Lorenzo Palma, A. Guidobaldi, A. D'Epifanio, S. Licoccia, T. Brown, A. Reale, A. Di Carlo, HOPV15, Rome, Italy, May 2015, B2.06.
- [88] H.-S. Kim, N.-G. Park, *J. Phys. Chem. Lett.* **2014**, *5*, 2927.
- [89] H. J. Snaith, A. Abate, J. M. Ball, G. E. Eperon, T. Leijtens, N. K. Noel, S. D. Stranks, J. T.-W. Wang, K. Wojciechowski, W. Zhang, *J. Phys. Chem. Lett.* **2014**, *5*, 1511.
- [90] A. Zakutayev, C. M. Caskey, A. N. Fioretti, D. S. Ginley, J. Vidal, V. Stevanovic, E. Tea, S. Lany, *J. Phys. Chem. Lett.* **2014**, *5*, 1117.
- [91] Q. Lin, A. Armin, R. C. R. Nagiri, P. L. Burn, P. Meredith, *Nat. Photonics* **2014**, *9*, 106.
-