TOPICAL REVIEW

Advances in modelling and simulation of halide perovskites for solar cell applications

Chol-Jun Yu

Chair of Computational Materials Design, Faculty of Materials Science, Kim Il Sung University, Pyongyang, Democratic People’s Republic of Korea

E-mail: cj.yu@ryongnamsan.edu.kp

Keywords: halide perovskites, solar cells, electronic structure, phonon, defects, interface

Abstract

Perovskite solar cells (PSCs) are attracting much attention as the most promising candidate for the next generation of solar cells. This is due to their low cost and high power conversion efficiency in spite of their relatively short period of development. Key components of PSCs are a variety of halide perovskites with ABX₃ stoichiometry, which are used as photoabsorbers. Their outstanding optoelectronic properties have brought breakthroughs in photovoltaic technology. To commercialize PSCs in the near future, however, these materials need to be further improved for better performance, represented by high efficiency and high stability. As in other materials development, atomistic modelling and simulation can play a significant role in finding new functional halide perovskites as well as revealing the underlying mechanisms of their material processes and properties. In this sense, computational work on the halide perovskites, mostly focusing on first-principles works, are reviewed with an eye to looking for ways to improve the performance of PSCs. Specific modelling and simulation techniques to quantify material properties of the halide perovskites are also presented. Finally, the outlook for the challenges and future research directions in this field is provided.

1. Introduction

As often highlighted in the media, the issue of climate change/global warming is one of the most serious global challenges that human beings face nowadays [1]. This is an inevitable result of the mass burning of fossil fuels to run factories, drive cars and operate buildings over recent decades. In fact, this has brought about the release of vast amounts of greenhouse gases, such as carbon dioxide (CO₂) and methane (CH₄), and caused another challenge for energy supplies due to the exhaustion of fossil fuel resources. To mitigate the catastrophic effects of global warming by reducing greenhouse gas emissions and to ensure sustainable energy supplies, more and more people and authorities are expressing a growing interest in renewable and clean (or low-carbon) energy sources, such that the majority of national and global energy policies include the exploitation of clean energy sources. Among several kinds of clean energy sources available around the globe, solar energy is the most promising source due to its abundance and eternal nature. Therefore, it is necessary to develop efficient techniques and devices for harnessing solar energy, which can contribute to resolving these environmental and energy challenges [2].

The most effective devices for harvesting solar energy are undoubtedly solar cells, invented in the 1960s, which convert solar light directly into electricity using the photovoltaic (PV) effect. So far, several kinds of solar cell have been developed and brought to market; as of 2015 the market share was 69.5% for single-crystalline (sc)-Si, 23.9% for polycrystalline (pc)-Si and 6.6% for thin-film pc-CdTe solar cells [3]. In fact, the most important factors determining the competence of solar cells in the market are power conversion efficiency (PCE), fabrication cost and device stability. According to the report by Green et al [4], certified PCEs of conventional PV modules are 28.8% for sc-GaAs, 24.4% for sc-Si, 19.9% for pc-Si, 18.6% for CdTe or Cu-In-Ga-Se (CIGS) alloy, and 13% for quantum dot and dye-sensitized solar cells. For these conventional solar cells, it is
difficult to achieve a high efficiency, low cost and high stability simultaneously; when the efficiency increases, the fabrication cost also increases. That is why sc-GaAs solar cells with the highest cost and high stability, and dye-sensitized solar cells with the lowest efficiency and low stability could not be commercialized. For the most widely used Si solar cells, however, both the efficiency and the cost are not sufficient to become competitive with fossil fuels in the electricity market. Therefore, it is our ardent desire to invent an innovative new type of solar cell with high efficiency, low cost and high stability.

In accordance with this desire, perovskite solar cells (PSCs) have emerged with an initial PCE of 3.8% in 2009 [5], and evolved rapidly to PCEs of over 10% within a few years [6–9]. After several years of intensive and extensive research, the efficiency has arrived at over 22% [10–12], which is an astonishing breakthrough in PV history when compared with the development periods of conventional solar cells mentioned above. Moreover, due to simple fabrication processes (low processing costs) and highly abundant raw materials (low materials costs) [13, 14], their fabrication costs are two thirds those of sc- and pc-Si solar cells, resulting in a short energy payback time and low overall CO₂ emission. Such huge success is mostly due to their key components, halide perovskites with a chemical formula of A(BX₃), where A and B are the monovalent (organic or inorganic) and divalent (metallic) cations, respectively, and X is the halide anion. These halide perovskites have been used as a solar light absorber and/or a charge carrier transmitter due to their optimal properties for these aims [15–24]. For instance, the archetype methylammonium lead iodide (CH₃NH₃PbI₃, MAPI hereafter), which was firstly employed in PSCs, has appropriate band gaps, optimal photovoltaic coefficients, weak exciton binding energies, high charge carrier mobilities, and long carrier diffusion lengths. However, there are still several fundamental issues to be addressed for the commercialization of PSCs: (i) high stability and long lifetime [25–29], (ii) scalability for large area modules [30] and (iii) low toxicity [31].

Atomistic modelling and simulation of materials have become essential in materials science, as they can provide valuable insights into known material processes and properties, and further predict the shortest route for finding new functional materials that meet requirements [2, 32, 33]. In particular, first-principles methods based on quantum mechanics can quantitatively determine most material characteristics of a crystalline solid, such as the lattice constants, electronic structure, linear response properties and transport properties, with a typical accuracy of 1% relative error to experiment, by using input data of only atomic information and known (or hypothetical) lattice structure. Being an interdisciplinary subject, the power of computational materials science can be supported in two aspects: (i) in hardware, rapid and ever-increasing processor speed and memory capacity, and (ii) in software, continuous progress in simulation algorithms and materials theory. As such, state-of-the-art atomistic modelling and simulation methods such as density functional theory (DFT), many-body perturbation theory and pair-wise interatomic potential molecular dynamics (MD) have been successfully applied to the halide perovskites. Recently, there have been several reviews of the theoretical research into halide perovskites: short reviews on the nature of chemical bonding [34] and on electronic and ionic motions [35], perspectives on the entropy [36] and on hybrid halide perovskites [37], and reviews focusing on MD simulations [38] and on optoelectronic properties [39, 40].

In this review, we inclusively discuss recent progress in first-principles atomistic modelling and simulation of halide perovskites in both hybrid organic–inorganic and purely all-inorganic forms. We focus our attention especially on how the calculated material properties can be linked with the performance of PSCs. Specific modelling and simulation techniques to elucidate the material properties of halide perovskites are also discussed. We consider the following material properties: (i) crystalline structures, (ii) electronic structures and optical properties, (iii) phonon dispersions and material stability, (iv) defect physics and ionic diffusion, and (v) surfaces and interfaces. The accuracies of calculations adopted in each work are also discussed in comparison with the available experimental data. Finally we present the challenges in the modelling and simulation of halide perovskites and future research directions.

2. Crystalline structures and polymorphism

The first step in solid-state modelling and simulation is to define the Bravais lattice (lattice constants and angles) and structural factor (atomic coordinates) of the unit cell. This can be done simply from experimental data such as those from x-ray diffraction (XRD) and scanning or transmission electron microscopy (SEM or TEM) with elemental analysis (e.g. energy dispersive x-ray spectroscopy (EDX or EDS)) for a known material, where data mining is a crucial tool to analyse large data sets [41] and to predict the structure–property cartograms [42]. Then, the initial structure is locally refined by performing structural optimization, which can provide a preliminary accuracy estimation of the adopted theoretical method by comparing the determined lattice constants with experimental data, and the supplementary information of elasticity (bulk modulus) by postprocessing the calculated data of total energy versus unit cell volume. If the structure is unknown, crystal structure prediction can be performed in different ways: (i) simply making a set of hypothetical crystalline
structures and then comparing their total energies, and (ii) global structure optimization using a variety of genetic and evolutionary algorithms [43, 44]. Once the refined structure is obtained, we can perform the chemical bonding analysis by measuring the bond length and bond angles, and proceed with further calculations for material properties to get the structure–property relationships.

2.1. Geometric factors for 3D halide perovskites

In the ABX₃ halide perovskite structure, the large monovalent cation A is bonded with the nearest twelve X halide anions, forming an AX₁₂ cuboctahedron, while the smaller divalent metal cation B forms corner-sharing BX₆ octahedra in a 3D framework. It should be noted that the A cation can be organic, forming hybrid organic–inorganic halide perovskites, and inorganic, leading to all-inorganic halide perovskites. At a glance, it seems that there are a great number of combinatorial cases simply with monovalent A and divalent B cations based on the periodic table. However, there are some geometric factors restricting the formation of stable 3D halide perovskite structures. The first is the Goldschmidt tolerance factor [45], \( t \), defined as,

\[
t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}
\]

where \( r_A, r_B \) and \( r_X \) are the ionic radii of the A, B, and X ions, respectively. It is empirically known that with \( t = 1 \) for a perfect cubic lattice, \( 0.8 \leq t \leq 1.0 \) for most stable perovskite structures with tetragonal, orthorhombic and rhombohedral (or trigonal) lattices. Otherwise, non-perovskite structures are formed: a hexagonal structure is formed when \( t > 1 \), and different structures are found when \( t < 0.8 \) [46, 47].

Regarding the halide ions (X = F⁻, Cl⁻, Br⁻, I⁻), typical examples of B-site metal cations are B = Pb²⁺, Sn²⁺, Ba²⁺, Ge⁴⁺, and monovalent A-site cations include organic CH₃NH₃⁺ (MA⁺), HC(NH₂)₂⁺ (FA⁺) and CH₃CH₂NH₃⁺ (EA⁺) cations and inorganic Cs⁺ and Rb⁺ cations. By using the calculated tolerance factors, Kieslich et al [48] demonstrated that 2352 amine–metal–anion compounds are possible, of which 180 halide compounds (and 562 organic anion-based compounds) can be stable perovskites with \( 0.8 < t < 1.0 \) (figure 1). These are too many cases to consider in computational work. In such a situation, another constraint factor is necessary.

The second constraint is known as the octahedral factor, defined as the ratio of the ionic radii of the B cation and the halide anion, \( \mu = r_B / r_X \) [49]. This reflects the stability of the BX₆ octahedron, and should be in the range of \( 0.44 \leq \mu \leq 0.9 \) for a stable perovskite. Together with the tolerance factor, the octahedral factor can provide a constraint to select stable halide perovskites among many possible cases. For instance, we can draw a 2D map of the ionic radii of A cations (Rb⁺, Cs⁺, MA⁺, FA⁺, EA⁺) and X anions (F⁻, Cl⁻, Br⁻, I⁻), which are marked along the abscissa and ordinate in figure 2, for typical B-site metal cations of Pb²⁺, Sn²⁺ and Ba²⁺. Their ionic radii with proper coordination numbers (CN = 12, 6, 6 for A, B, X ions, respectively) are provided in [50, 51]. In figure 2, we can see the intersections located within the polygonal (shaded) region formed by tolerance limits of these constraint factors, which indicate a potentiality of stable perovskite formation with corresponding A, B, X elements, and those outside the region, which indicate a failure of perovskite formation. It should be noted that there is an ambiguity in defining ionic radii due to the nonsphericity of the organic molecular A cation and the reduced electronegativity of heavy halide anions, and thus some modifications have been proposed, such as effective molecular A cation radii [48] and modified B-site metal cation radii from empirical bond lengths [47].
2.2. Octahedral tilting or distortion and polymorphism

Once a certain compound with ABX₃ formula is proven to form a stable halide perovskite due to its appropriate tolerance and octahedral factors, we should also consider the possibility of modification in the shape of BX₆ octahedra. In fact, BX₆ octahedra can be tilted or distorted because of the slight rotation or displacement of constituent atoms or molecules at finite temperature (and possibly pressure). It is worth noting that octahedral tilting is known to be associated with antiferroelectricity, while octahedral distortion caused by cation off-centring yields ferroelectricity (i.e. the creation of spontaneous electric polarization) that can enhance charge carrier separation and allow the photovoltage to exceed the band gap thousands of times over [52, 53]. Such octahedral tilting or distortion may lose the symmetry of a crystalline unit cell, being closely related with phase transition driven by temperature [54]. In general, the archetype cubic perovskite structure is observed at high temperature, and when temperature decreases, lower symmetry phases are found in the order of tetragonal → orthorhombic → monoclinic and/or rhombohedral.

For the typical case of hybrid organic–inorganic halide perovskite MAPI, which has been playing a major role in advancing PSC technology, its cubic α-phase with space group Pm̅3m is only found at high temperature, and phase transition to the tetragonal β-phase (I4/mcm) occurs at 327.4 K, and to the orthorhombic γ-phase (Pna2₁) at 162.2 K [55]. In the case of MAPI, the orientation of the MA cation is of great importance in determining the octahedral tilting and the crystalline phase [53, 56]. The organic MA⁺ cation has two modes of reorientation: (i) methyl and/or ammonium rotation around the C–N axis and (ii) whole molecular rotation of the C–N axis itself [53]. In the cubic phase, three different orientations are identified as (100), (110), and (111) for the C–N axis, which lower lattice symmetry from the cubic Pm̅3m to the pseudocubic Pm and R3m phases, and the (110) model was found to be the most energetically stable configuration by ab initio MD [56] and structural optimization [57] in agreement with experiment [53]. By performing ab initio MD simulations, the activation barriers were calculated to be 117 meV for reorientations of the axis [58] and 13.5 meV for ion rotation [59, 60]. For the tetragonal phase, the C–N bonds in MA distribute in a vertical way, and in a parallel way for the orthorhombic phase, as shown in figure 3. In these non-cubic phases, their unit cells (\(\sqrt{2} a \times \sqrt{2} a \times 2a\) supercell) contain four formula units (48 atoms), being larger than the cubic phase with one formula unit (12 atoms) [61].

Temperature-driven phase transitions were also observed for all-inorganic halide perovskite ABX₃ (A = Cs, Rb; B = Pb, Sn; X = F, Cl, Br, I) (see [62] and references therein). For CsSnI₃, typically, phase transitions from the perovskite cubic α-phase (Pm̅3m2m) upon decreasing temperature occur to the tetragonal β-phase (P4/mnm) at 446 K and to the orthorhombic γ- and non-perovskite Y-phases (Pnma) at 373 K [63], while for CsPbI₃, phase transition occurs only to the non-perovskite orthorhombic Y-phase at 583 K [64]. It is worth noting that for CsSnI₃, two orthorhombic structures coexist at room temperature, of which the yellow Y-phase characterized by an edge-connected 1D double-chain is not useful for solar energy applications [65]. Unlike the hybrid perovskite, the all-inorganic halide perovskites do not have rotational molecular disorder in the A-site, and instead the flexibility associated with the inorganic octahedra network solely causes the phase transition. By performing the phonon calculations for CsBX₃ (B = Pb, Sn) in cubic phase, Yang et al [62] revealed that these inorganic halide perovskites exhibit lattice instabilities in the cubic phase, confirmed by the phonon soft mode (imaginary frequencies) at the Brillouin zone boundary, and thus the octahedral tilting and distortion that is by
definition antiferroelectric in nature can occur spontaneously. A quantitative picture for phase diversity can be obtained by calculating the free energy through phonon calculations, which will be discussed later.

2.3. Low dimensional and double lead-free halide perovskites
With respect to the environmental impact, there is concern about the toxicity of lead in the major halide perovskites such as MAPI and CsPbI₃, promoting an extensive search for alternatives. Although there has been extensive research to try simple substitution of Pb²⁺ in the ABX₃ structure with alternative divalent cations, it has turned out to be challenging. There is also research interest in another approach to search for multivalent elements. This resulted in low-dimensional perovskite structures such as A₃B-II X₉(3–2–9) layered (2D), A₁B-II X₅(3–1–5) single-chained (1D) and A₁B-II X₆(4–1–6) isolated octahedra (0D), and double perovskite structures A₂B-I B-II X₆(2–1–1–6) [66, 67]. Xiao et al [68] have reported their recent work on Pb-free halide perovskites with such different structural dimensionalities, which have a wide range of band gaps and PCEs. In particular, 3D double perovskites such as Cs₂AgBiX₆ (X = Br, Cl), called elpasolites, have received much attention as promising absorber materials [69–73]. Volonakis et al [74] have reported a series of double perovskites with B= Cu, Ag, Au and B= Bi, Sb, predicting their band gaps in the range from 0.5 to 2.7 eV for the Bi system and from 0.0 to 2.6 eV for the Sb system. So far, there has been no report for double perovskite-based solar cells, which might be due to difficulties in synthesizing uniform thin films of the correct phase and chemical composition.

2.4. Solid solutions
There is an ever-increasing need to improve the performance of solar cells, represented by higher efficiency and greater stability. Although the PCE of MAPI-based solar cells can be as high as 22%, being comparable with sc-Si solar cells, their instability in air is relatively low, which could be a major barrier to commercialization. Making solid solutions or mixing at the A-site and/or X-site with two or more similar elements is an efficient way to satisfy the need for enhancing performance by increasing the stability, improving the charge carrier transport, and tuning the band gap [31, 75]. Experimentally, it is much easier to realize such mixing than to prepare double perovskites. There have been several first-principles investigations into perovskite solid solutions such as hybrid
perovskites, MAPb\((I_{1-x}Br_x)_3\) [57, 76–78], MAPb\((I_{1-x}Cl_x)_3\) [79] and (Cs/MA/FA)PbI3 [80], and inorganic perovskites, CsPb\((X_{1-x}Y_x)_3\)\((X, Y = I, Br, Cl)\) [81] and \((Rb,Cs_{1-x})SnI_3\) [82]. When mixing larger I\(^-\) anions with smaller Br\(^-\) or Cl\(^-\) anions, the crystalline lattice can be reduced and a phase transition from the tetragonal to the cubic can occur at room temperature. Meanwhile, mixing MA\(^+\) cations with larger FA\(^+\) cations can tune the octahedral tilting with the proper Goldschmidt tolerance factor.

To perform modelling of solid solutions, we can use the supercell (SC) method, with the sacrifice of high computational cost. When employing the pseudopotential plane wave method, the virtual crystal approximation (VCA) approach can be used as an alternative, to reduce the computational cost, but the accuracy or reliability should be checked carefully before going into the main calculation. In the VCA approach, the virtual atom is introduced and its pseudopotential is constructed by averaging the relevant potentials and wave functions of constituent atoms [83, 84]. There are some technical problems with these methods: random distribution of alloying atoms for the SC method, and local effects from the interactions between the constituent atoms for the VCA method. It has been proven that the VCA approach can reliably reproduce the lattice constants in cubic phase as a linear function of mixing content, i.e. Vegard’s law, for hybrid halide perovskites [78, 79] (figure 4).

3. Electronic and optical properties

Since the halide perovskites are typically used as a light absorber in most applications, the electronic and optical properties are of primary importance. After modelling the crystalline solid using a unit cell or supercell and refining their cell by performing the structural optimization, the electronic energy band structure and the corresponding density of states (DOS) can be obtained by non-SCF calculation. Postprocessing the energy band produces directly the effective masses of charge carriers (conductive electrons and holes). Other optical properties such as exciton binding energy and photoabsorption coefficients are determined by using the frequency-dependent dielectric constants, which can be routinely calculated within density functional
perturbation theory (DFPT) [85–87] without or with the effect of electron–hole interaction by using the Bethe–Salpeter approach [88].

### 3.1. Spin–orbit coupling (SOC) and many-body effects

In general, standard DFT exchange-correlation (XC) functionals within local or semi-local approximations, such as local density approximation and generalized gradient approximation (GGA), severely underestimate the band gap of inorganic semiconductors, due to the inherent nature of DFT as a ground state theory and the artificial self-interaction between electrons, although they can provide reliable structures and stabilities. Surprisingly for MAPI, the GGA functionals (Perdew–Burke–Ernzerhof (PBE) [89] or PBE for solid: PBEsol [90]) can yield a band gap in excellent agreement with experimental values within ±0.1 eV [77–79, 91]. This is due to a fortuitous error cancellation between the GGA underestimation and the overestimation by the lack of SOC [92–96], which inversely indicates the importance of relativistic effects in halide perovskites. From analysis of the partial density of states (PDOS) for halide perovskites ABX₃, the valence band maximum (VBM) consists of an antibonding coupling of X p-states and B s-states, while the conduction band minimum (CBM) is dominated by B p-states (see figure 5). It should be noted that for MAPI the majority of occupied molecular orbitals of MA are found deep (∼5 eV) below the VBM and a minority (but not negligible amount) are found ∼0.5 eV below the VBM, indicating hydrogen bonding interactions between the organic MA moiety and the inorganic PbI₆ octahedra [97]. In APbX₃ perovskites the heavy Pb atom has a significant SOC effect of lowering the CBM, whereas the lighter Sn atom has a relatively weak SOC effect, resulting again in the large underestimation of the band gap by GGA functionals for ASnX₃ perovskites [98, 99]. Moreover, the GGA functionals cannot accurately describe dispersion of the valence band even in Pb-based perovskites.

The relativistic effect can be approximated by first-order scalar relativistic (SR) and higher order SOC contributions. Umari et al [97] demonstrated that SR-DFT barely changes the band obtained by DFT, while SOC-DFT largely lowers the conduction bands for hybrid iodide perovskites MAPbI₃ and MASnI₃. When the SOC effect is considered, splittings of the conduction bands, known as the Rashba effect, occur as a result of interaction between the magnetic moment (spin) of the electron and the local electric field [100]. In fact, this electromagnetic force displaces electrons in the momentum space, acting on up and down spins in opposite directions. For the case of cubic halide perovskites, neglecting SOC yields direct band gaps at the band edge points of R and M in the Brillouin zone, as shown in figure 6. When SOC is turned on, both the valence and conduction bands around R split into symmetrical valleys for the case of MAPI (see figure 6(a)). More importantly, since the splitting is much more evident in the Pb 6p conduction band compared with the I 5p

---

**Figure 5.** Partial DOS for (a) MAPbI₃ and (b) CsPbI₃ in cubic phase, calculated by the pseudopotential plane wave method. The VBM is set to be zero.
valence band, the CBM slightly shifts along the $R \rightarrow \Gamma$ line, resulting in a vertical energy difference of 25 meV between the CBM and VBM at the R point \[94\.\] Thus the band gap changes into the indirect mode, which affects light absorbing function as we will discuss later. Motta et al \[94\] revealed that the orientation of the MA molecular cation has the same effect on the band gap transition. For the all-inorganic halide perovskites like CsPbI$_3$, however, such relativistic spin-splitting does not occur due to a centre of inversion symmetry. Although the SOC effect causes the separation of Pb 6p into $p_{1/2}$ and $p_{3/2}$, no splitting of the band extrema is observed at the high symmetry points, as shown in figure 6(b).

Since both the standard DFT and SOC treatment based on local or semi-local XC functionals are insufficient to describe the electronic structures of halide perovskites, it is necessary to adopt more delicate approaches. One way is to use a screened hybrid functional such as HSE06 \[101,\ 102\], which has a tendency to overestimate the band gap of hybrid and all-inorganic perovskites, and thus by combining with SOC treatment can give a reasonable estimation. More profoundly, as in other inorganic semiconductors, an accurate description of electronic structure can be provided by considering many-body interactions within the $GW$ approximation \[97,\ 103,\ 104\] or within the random phase approximation (RPA) \[105\]. The quasiparticle self-consistent $GW$ (QSGW) approach could yield the large overestimation of band gaps as 2.68 $\sim$ 2.73 eV (1.55 eV) for MAPI (MASnI$_3$), while SOC + $GW$, by combining with SOC can give the closest band gaps of 1.67 eV (1.10 eV) to the experimental value of 1.60 eV (1.20 eV) \[97,\ 103\]. In addition, inclusion of SOC in the $GW$ calculation increases band dispersion so significantly that the standard parabolic approximation can no longer be applied to the band extrema, which differs from experimental results indicating parabolic band extrema in MAPI.

### 3.2. Tuning band gap by substitution and mixing

As the key factor in light absorbing properties, the band gap of the halide perovskites can be tuned by different means: (i) static volume change, (ii) temperature change, and (iii) chemical substitution. When decreasing the volume by the action of a small perturbation or by increasing pressure, the band gap was found to monotonically decrease in DFT calculations with the additional benefit of transition from indirect to direct band gap for MAPI \[106,\ 107\]. Also, it was found that the out-of-phase band-edge states are stabilized as the lattice expands \[60\].

Regarding the temperature effect, there has been no theoretical work carried out yet, although the band gap was observed in temperature-dependent photoluminescence to decrease with decreasing temperature from 1.61 eV

---

**Figure 6.** (a) Electronic energy band of hybrid iodide perovskite MAPbI$_3$ in cubic phase around R point without (left panel) and with (right panel) SOC. Adapted from \[94\]. CC BY 4.0. (b) Band structure of all-inorganic iodide perovskite CsPbI$_3$ in cubic phase without (dashed lines) and with (solid lines) SOC. VBM is set to be zero. High symmetry points and lines in the Brillouin zone are shown.
at 300 K to 1.55 eV at 150 K for MAPI [108]. We focus on the third method of chemical substitution at each site of ABX₃, which is more appropriate for materials design than the physical volume effect [34, 109, 110].

The A-site cation of MAPI can affect only indirectly the band gap by changing the crystal structure due to its molecular orbitals far away from the VBM. When replacing the MA cation with a smaller molecular cation such as NH₄⁺ or H⁺, the band gap was found to lower by 0.3 eV with contraction of cubic lattice from 6.29 to 6.21 Å in the QSGW + SOC calculation for NH₄PbI₃ [103], and to be less than 0.3 eV with a lattice constant of 6.05 Å for HPbI₃ [60]. It is important to recognize the relationship between the ionic radii and the local structure. In fact, both NH₄PbI₃ and HPbI₃ adopt non-perovskite chain or layer structures due to their tolerance factors of lower than 0.81, which give rise to instability of the octahedral networks with respect to tilting. Replacing MA with the former case of MA, Rb, Cs, or H⁺ can also result in structural distortions due to their tolerance factors of lower than 0.81, which give rise to instability of the octahedral networks with respect to tilting. Replacing MA with the larger FA can also result in structural distortions [111]. Meanwhile, substituting inorganic cation Cs⁺ with a smaller ionic radius leads to a widening of the band gap to 1.73 eV in cubic CsPbI₃ [112–114], being suitable for the top cell material in a tandem cell. However, it is difficult to form its cubic phase at room temperature. In this situation, it is desirable to adopt the mixing technique, which can promise the synergistic effect of enhancing stability against moisture and maintaining efficiency. Mixing can be done in various ways, such as MA/FA, Cs/MA, Rb/Cs [82], Cs/MA/FA [80], and Rb/Cs/MA/FA [115].

Substitution or mixing on the B-site can directly alter the conduction band dominated by B p-states without the severe change in crystal structure. For example, replacing Pb with isovalent Sn in MAPI reduces the band gap by ~0.3 eV due to a slight downward shift of the CBM since the Sn 5p-states are weaker than the Pb 6p-states [116]. It also induces a phase transition from the tetragonal I4 cm phase for MAPI to the pseudocubic P4 mm phase for MAxSn₁₋ₓI₃, being beneficial to the light absorber. However, Sn³⁺ is less chemically stable in the octahedral network due to its ease of oxidation to Sn⁴⁺, resulting in the degradation of PSCs. Another isovalent Ge²⁺ is further unstable owing to the lower binding energy of its 4p electrons. When mixing Pb with Sn to form solid solutions MA(Sn₁₋ₓPbₓ)I₃, the band gap was found to follow the quadratic function of mixing content x (see figure 7), such that a band inversion occurred associated with a systematic change in the atomic orbital composition of the conduction and valence bands [116–118].

Since the X-site anion dominates the valence bands, its substitution can be expected to change the VBM [119]. In going from I to Br to Cl, the valence band composition changes from 5p to 4p to 3p, resulting in a monotonic increase in electron binding energy (higher ionization potential). Accordingly, the band gap increases from 1.5 eV for MAPI to 2.10 eV on Br [78] to 2.70 eV on Cl substitution [79]. For the case of FAPbX₃, the substitution of Br for I increases the band gap from 1.48 to 2.23 eV as found in experiment [120]. For the former case of MA(Sn₁₋ₓPbₓ)I₃, mixing I with Br or Cl can give band gap changes according to the quadratic function of mixing content (figure 7),

\[ E_g(x) = E_g(0) + [E_g(1) - E_g(0) - b]x + bx^2 \]  \tag{2}

where \( b \) is the bowing parameter reflecting the fluctuation degree in the crystal field and the nonlinear effect from the anisotropic binding [78, 79, 121]. If the bowing parameter is zero, the band gap could follow Vegard’s law, as with the lattice constant. Comparing MAPb(I₁₋ₓBrₓ)I₃ and MAPb(I₁₋ₓClₓ)I₃, they are 0.185 eV (0.33 eV in experiment [121]) and 0.873 eV respectively, indicating the larger compositional disorder and low miscibility for the latter case (figures 7(b) and (c)).
3.3. Transportation of charge carriers

In the halide perovskites, the major charge carriers are conduction electrons and holes created by several external factors. They can couple with each other by an electrostatic interaction to form a kind of quasiparticle, namely an exciton. Therefore, the effective masses of these charge carriers and the exciton binding energy are of importance in checking the suitability for the charge transport layer in solar cells.

Effective masses of conduction electrons and holes can be calculated from the lower conduction band and upper valence band near the R point for the cubic phase, which can be approximated as a parabolic function of momentum \( k \) as follows

\[
E = \frac{\hbar^2}{2m^*} k^2 \Rightarrow \quad m^* = \frac{\hbar^2}{2} \left( \frac{\partial^2 E}{\partial k^2} \right)^{-1}. 
\]  

This parabolic approximation can be slightly broken when considering the SOC effect in the hybrid halide perovskites as discussed above. Therefore, the calculated effective masses depend somewhat on the theoretical method and the complexity of band dispersion. The \( GW + \) SOC calculation yielded average values of \( m_e^* / m_e = 0.19 (0.28) \) and \( m_h^* / m_e = 0.25 (0.13) \) for cubic MAPI (MASnI_3) [97], whereas PBE with the inclusion of a van der Waals (vdW) correction [122] can give similar values of \( m_e^* / m_e = 0.20 (0.34) \) and \( m_h^* / m_e = 0.23 (0.43) \) for MAPI (MAPbCl_3) [61, 79]. The electron effective masses are larger than those of GaAs (0.07) and CdTe (0.11), whereas the holes have distinctly lower masses (0.5 and 0.35, respectively), predicting a high hole mobility in the hybrid halide perovskites. For the cubic CsSnX_3, the hole effective masses were predicted to decrease when going from Cl to Br to I by QSGW calculations [104]. Since the mobility is inversely proportional to the effective mass, the halide perovskites are expected to exhibit ambipolar and large diffusion lengths for electrons and holes [95].

An exciton can be viewed as a H atom with differences attributed to (i) a replacement of the electron and nucleus masses by the effective masses and (ii) an introduction of a dielectric constant, \( \varepsilon \), of the material. Then, the exciton binding energy can be obtained using the effective masses and dielectric constant in the following equation

\[
E_b = \frac{m_e \varepsilon^4}{2(4\pi\varepsilon_0)^2 \hbar^2} \frac{m_e^* + m_h^*}{m_e} \frac{1}{\varepsilon^2} \approx 13.56 \frac{m_e^*}{m_e} \frac{1}{\varepsilon} (\text{eV}) 
\]  

where \( m_e^* (1 / m_e^* = 1 / m_e^* + m_h^*) \) is the reduced effective mass. The static dielectric constant can be calculated by the DFPT method without or with electron–hole coupling, as will be discussed below. If this modelling is valid as the extending radius of the lowest bound state \( r^* = \varepsilon m_e^* a_B \), where \( a_B \) is the Bohr radius, the exciton is the weak exciton, known as the Mott–Wannier exciton. Otherwise, it is a Frenkel exciton, being extremely localized. For MAPI (MAPbBr_3), the exciton binding energy \( E_b \) and effective radius \( r^* \) were calculated to be 45 (99) meV and 3.0 (1.9) nm [78], indicating that the excitons are likely to be of the Mott–Wannier type.

Charge carrier transport can be characterized by the diffusion length \( L_D \) defined as the average length a carrier travels before recombination. This can be calculated using the diffusivity \( D \) and charge carrier lifetime \( \tau \) by \( L_D = \sqrt{D\tau} \). The diffusivity can be directly related to mobility \( (\mu) \) by the Einstein relation \( \mu = Dq/k_BT \) due to the fact that transport is limited by carrier scattering and carrier effective mass. \( L_D \) must be long enough for the charge carriers to reach the contacts in solar cells, and these are reported to be considerably longer in MAPI than in other semiconductors. This can be partly attributed to the defect–tolerance of hybrid halide perovskites [123].

Providing effective masses of \(<0.2m_e\) for MAPI, the carrier mobility was calculated to be modest \(<100 \text{cm}^2/(V \cdot \text{s})\) compared to the inorganic semiconductors Si or GaAs \(>1000 \text{cm}^2/(V \cdot \text{s})\) [124]. Such limitation of carrier mobility can be caused by strong scattering. Zhao et al. [125] have found that by applying the PBE + SOC approach the electron–acoustic phonon couplings in MAPI are weak, and charge carriers are scattered predominantly by charged defects or impurities.

3.4. Dielectric constant and photoabsorption coefficient

The frequency-dependent complex dielectric functions can be calculated within DFPT without the electron–hole coupling effects. Although such excitonic effects can be calculated by solving the Bethe–Salpeter equation for the two-body Green function without or with local field effect [126], ignoring electron–hole coupling still yields a reasonable result in good agreement with experiment for the small band gap semiconductors [88].

Given a self-consistent QSGW potential, the polarizability \( P(q, \omega) \) is obtained using the RPA, and then the inverse dielectric function is obtained from \( \varepsilon^{-1} = [1 - \nu(q)P(q, \omega)]^{-1} \) where \( \nu(q) \) is the bare Coulomb interaction [127]. The macroscopic dielectric function \( \varepsilon_M \) is given as follows
Then, the frequency-dependent photoabsorption coefficient is given as

$$\alpha(\omega) = \frac{2\omega}{c} \sqrt{\frac{[\text{Re}^2 \varepsilon_M(\omega) + \text{Im}^2 \varepsilon_M(\omega)]^{1/2} - \text{Re}\varepsilon_M(\omega)}}{2}.$$  

Figure 8 shows the macroscopic dielectric functions and the photoabsorption coefficients as functions of photon energy in hybrid halide mixed perovskites MAPb(I$_{1-x}$Cl$_x$)$_3$, calculated using PBE + vdW-D2 functional within VCA as the mixing content $x$ increases [79]. The real part is related to the polarizability of the medium in response to an oscillating electric field. For the hybrid solid solutions MAPb(I$_{1-x}$Br$_x$)$_3$ and MAPb(I$_{1-x}$Cl$_x$)$_3$, the static dielectric constants decrease as the mixing content $x$ increases [78, 79]. The rotation of molecular cation MA$^+$ is of some importance in the explanation of these variation tendencies. In fact, the static dielectric constant, $\varepsilon_M = \lim_{q \to 0} \frac{1}{q} \varepsilon_{G=0,G'=0}$

$$\varepsilon_M = \lim_{q \to 0} \frac{1}{q} \varepsilon_{G=0,G'=0}$$

is dominated by the rotational motion of the MA molecule that has an intramolecular dipole, while the high-frequency or optical dielectric constant, $\varepsilon_\infty \approx \varepsilon_M(\omega \sim 10^{13}$ Hz) is related to the vibrational polar phonons of the lattice (see figure 8(c)) [92]. The MA molecular dipoles screen the Coulombic interaction between photo-excited electrons and holes in the Pb–I sublattice [128–130], leading to a reduction of exciton binding. The MA cation is situated in a cuboctahedral cage, and thus, when going from I to Br to Cl, the size of the cage decreases, inducing a restriction on molecular motion and a decrease in static dielectric constant with a reduction of exciton screening. In accordance with these tendencies, the onset of photoabsorption and the first peak shift to a higher photon energy, i.e. shorter wavelength light, with increasing mixing content. There exist other first-principles calculations of optical properties for CsSnI$_3$ [131], CsPbX$_3$ [132], MASnX$_3$ [133] and MABA$_3$ [134].
4. Phonon and material stability

Crystalline materials in general exhibit phase transitions upon changing temperature and pressure. A certain phase with a specified crystal structure can exist in a stable state in a certain range of temperature and pressure, and at the critical value, changes into another phase. Such stability in the thermodynamic conditions is called phase stability. On the other hand, crystalline materials can be chemically decomposed into several components, which may be in crystalline and/or gaseous states. This is called chemical stability. During such chemical decomposition, heat can be generated (exothermic reaction) or absorbed (endothermic reaction). For the former case, the chemical decomposition can occur spontaneously, being intrinsic chemical instability that can be considered under different thermodynamic conditions, while for the latter case the reaction can be triggered and progressed with extrinsic factors such as moisture, light and heating; this is extrinsic chemical instability. Both the phase stability and the intrinsic chemical instability under certain thermodynamic conditions can be predicted by performing phonon calculations to determine the entropy [36].

The Gibbs free energy of a compound as a function of temperature \( T \) and pressure \( P \) is given as

\[
G(T, P) = F(T, V) + PV
\]  

where \( F(T, V) \) is the Helmholtz free energy as a function of temperature and volume \( V \). For the \( PV \) term, the total energies are calculated by varying the unit cell volume, fitting into the empirical equation of state for a solid [135] to obtain the \( E(V) \) function, and then the pressure is estimated by conducting differentiation \( P = -(\partial E/\partial V)_T \) [136]. Within the adiabatic approximation, \( F(T, V) \) can be separated into ionic vibrational and electronic contributions [85, 137],

\[
F(T, V) = F_{el}(T, V) + F_{el}(T, V) \simeq F_{el}(T, V) + E(T = 0 \text{ K}, V).
\]  

In the electronic Helmholtz free energy, \( F_{el}(T, V) = E(T = 0 \text{ K}, V) - T S_{el} \), the \( T S_{el} \) term is ignored because the electronic temperature effect is negligible for nonmetallic systems in the room temperature vicinity [138]. Within the quasiharmonic approximation (QHA), the ionic term \( F_{el} \) can be calculated as follows [136, 137]

\[
F_{el}(T, V) = 3Mk_B T \int_0^{\omega_{V}} \ln \left\{ 2 \sinh \left( \frac{\hbar \omega(V)}{2k_B T} \right) \right\} g(\omega) d\omega
\]  

where \( \omega(V) \) is the phonon frequency as a function of volume, \( M \) is the atomic mass, \( g(\omega) \) is the normalized phonon DOS and \( \omega_{V} \) is the maximum of the phonon frequencies. The phase stability or chemical intrinsic stability can be estimated by the Gibbs free energy difference between the two phases or the products and the reactants.

4.1. Phonon dispersion and phase stability

It is crucial to get a precise insight into phonon dispersions in the halide perovskites in order to understand material processes such as ionic transport, and the recombination and scattering of charge carriers, as well as material stabilities. Phonon dispersion is computationally accessible via lattice dynamics calculations, in which the dynamic matrix is constructed via the Hessian matrix as the second derivatives of the total energy with respect to the atomic displacements that can be obtained directly from DFT calculations. The Hessian matrix or interatomic force constants can be calculated either in real space by performing force calculations on a series of symmetry-inequivalent displaced structures with the use of a supercell [139, 140] or in reciprocal space using perturbation theory (e.g. DFPT [85]). Diagonalizing the dynamic matrix yields a set of eigenvectors (phonon modes) and eigenvalues (phonon frequencies) [36]. Lattice dynamics in DFT is one of the most expensive calculations and, thus, classical or semi-classical MD based on interatomic potential functions [141] can be used to overcome the limitations of DFT.

For the hybrid perovskite MAPI in the cubic, tetragonal and orthorhombic phases, the phonon bands were calculated in the harmonic approximation [142, 143]. Confirming that the calculated phonon spectra were in quite good agreement with the experimental data, these calculations indicate that the lowest bands below 100 cm\(^{-1}\) are assigned to the bending and stretching of the Pb–I bonds, i.e. diagnostic modes of the inorganic cage. The medium bands in the range from 100 to 150 cm\(^{-1}\) are the modes coupled to the molecular motion, and the highest frequency branches in the range from 300 to 3300 cm\(^{-1}\) are associated with the vibration and bond stretching of the MA cation. For other hybrid halide perovskites MAPbX\(_3\) (X = Br, Cl), similar arguments were found to be valid, putting special emphasis on the reorientation of the MA cations, which plays a key role in shaping the vibrational spectra of the different compounds [53, 144–146]. It was found that MAPI exhibits double-well instabilities at the Brillouin zone boundary and a remarkably short phonon quasiparticle lifetime, being associated with low thermal conductivity. Also, the optical phonon scattering is stronger than the acoustic scattering at room temperature in these materials [52, 145, 147]. Vibrational entropy was proved to play a crucial role in determining the stable phase, e.g. between the pseudocubic and tetragonal phase for MAPI, such that the
materials favor structures that maximize the number of soft intermolecular interactions as temperature rises [148].

It is important to understand the anharmonic effects in the phase transition of halide perovskites. When the potential energy of a crystalline solid is expanded as a Taylor series of ionic displacements, only the second term $(d^2U/dr^2)$ is considered in the harmonic approximation with the temperature-independent frequencies and infinite lifetime, while the effects of temperature and first-order anharmonicity can be considered in the QHA [150]. It is associated with the imaginary (or negative) frequency, i.e. soft mode. While all the phonon modes have positive frequencies in the tetragonal and orthorhombic phases (figure 9(a)), there are two imaginary frequency acoustic modes in the cubic phase, of which the centres are around the $p[(1/2, 1/2, 0)]$ points, corresponding to the $\{111\}$ and $\{110\}$ directions (figure 9(b)). As a common feature of the perovskites, these soft modes indicate a double-well characteristic in the potential energy surface, and thus a dynamic instability of the cubic structure as observed in inelastic x-ray scattering measurements [52]. Such instabilities represent antiferroelectric distortions associated with collective rotation and tilting of the corner-sharing octahedral framework that can be observed directly in MD [59, 151]. In the double-well potential, the cubic phase is a saddle point between two equivalent broken-symmetry phases (figure 9(d)), and the barriers are 37 and 19 meV for the R and M modes, being comparable to $k_BT$ at room temperature [147]. The phase transitions from cubic structure can be understood as a condensation of these soft modes, as proved by solving the time-dependent Kohn–Sham equation describing the nuclear motion in the double-well potential [147, 152, 153].

The soft phonon modes are also found in the all-inorganic halide perovskites. For the case of CsSnI₃ perovskite, the temperature-dependent lattice dynamics were carried out for the four different phases within the QHA, revealing the strong anharmonic effects such as soft modes [65, 154]. However, the calculated phase transition temperatures fail in quantitative agreement with experimental values, requiring further studies to eliminate these discrepancies. Yang et al [62] systematically investigated the phonon dispersions of CsSnX₃ and CsPbX₃ ($X = F, Cl, Br, I$) perovskites, verifying the phase instabilities of cubic structures related to the spontaneous octahedral tilting. In all eight cases, double-well potentials as a function of distortion amplitude $Q$, given by

\[
E(Q) = aQ^2 + bQ^4 + O(Q^6)
\]  

Figure 9. Phonon dispersions and density of states for (a) orthorhombic and (b) cubic MAPbI₃, reprinted figure with permission from [147], copyright 2016 of the American Physical Society, (c) cubic CsPbI₃, adapted from [149] with permission of the Royal Society of Chemistry, and (d) double-well potential with a saddle point corresponding to the cubic phase and two local minima, adapted from [52] with permission of the American Chemical Society.
with fitting parameters $a$ and $b$, were found for soft phonon modes with barrier heights ranging from 108 to 512 meV, assessing the chemical and thermodynamic driving forces for these instabilities. When compared with the hybrid halide perovskites, it is surprising that the soft mode is found even at the zone centre point $\Gamma$ (figure 9(c)), which is related to the ferroelectric distortion. Marronnier et al [155, 156] thoroughly investigated this anomaly at $\Gamma$ for the cubic and tetragonal phases of CsPbI$_3$. As a polar mode, the soft phonon mode found at $\Gamma$ for cubic CsPbI$_3$ is linked to the displacements of the Cs$^+$ cation in one direction and of the $\Gamma^-$ anion in the opposite direction. In spite of such displacements, ferroelectricity has not been observed at a macroscopic scale due to the oscillations along this polar soft mode. Volume relaxation with tight convergence thresholds ($10^{-4}$ Ry Bohr$^{-1}$ for the force and $10^{-14}$ for the phonon self-consistency) and frozen phonon calculations remove the soft modes at $\Gamma$. Based on those results, it was concluded that the strongly anharmonic mode at $\Gamma$ will not condense at lower temperatures, whereas the remaining phonon instabilities at the edge points of M and R are responsible for soft modes that condense at lower temperatures to induce the phase transition [155].

4.2. Thermodynamic miscibility in solid solutions

Forming solid solutions or alloys by mixing two or three equivalent elements at the same site can provide a direct and easy route to improving the performance of materials. As such, perovskite solid solutions were found to have a controlled band gap and improved stability; in lead-based hybrid halide perovskites APbX$_3$, the best efficiency can be obtained by mixing organic cations (MA/FA) on the A-site and halides on the X-site. In such mixing cases, it is important to understand whether the solid solution is stable against phase separation in the entire range of composition, where configurational entropy can play an important role in describing the disorder of site occupancy [36, 77]. Thermodynamic miscibility for mixing two components, e.g. $(1 - x)$ABX$_3$ + $x$A$'_B$X$_3$, can be calculated by the Helmholtz free energy difference given as

$$\Delta F(x, T) = \Delta U(x, T) - T\Delta S(x).$$

(11)

The first term, internal energy difference, is written as follows [157]

$$\Delta U(x, T) = \sum_k \Delta U_k(x) g_k e^{-E_k(x)/k_BT}$$

$$\sum_k g_k e^{-E_k(x)/k_BT}$$

(12)

$$\Delta U_k(x) = E_k(x) - [(1 - x)E_{ABX_3} + xE_{A'BX_3}]$$

(13)

where $E_k(x)$ is the DFT total energy of the alloy with mixing content $x$ and configuration number $k$, and $g_k$ is the degeneracy representing the number of configurations with the same energy $E_k$. At room temperature, the internal energy of mixing can be well fitted into the subregular solution expression [76, 157]

$$\Delta U(x) = \Omega x (1 - x), \quad \Omega = \alpha + \beta x$$

(14)

with the fitting parameters, $\alpha$ and $\beta$. Then, the entropy of the alloy is given in the ideal solution limit as follows

$$\Delta S(x) = -k_B [x \ln x + (1 - x) \ln(1 - x)]$$

(15)

which is expected for a random alloy at high temperatures.

Brivio et al [76] have provided the thermodynamic insight for photoinstability in the hybrid halide solid solutions MAPb$_{(1-x)}$Br$_x$$_3$. By generating different configurations (using the SOD code [158]) and applying the generalized quasichemical approximation method [159], they calculated the internal energy, configurational entropy, Helmholtz free energy of solid solutions and phase diagram as functions of the alloy composition (figure 10). At low temperatures, the free energy curve is asymmetric and positive, indicating the existence of a miscibility gap. When the temperature increases, the curve becomes symmetric and negative since the probability of sampling all possible configurations increases. From the calculated phase diagram, it is clear that there exists a stable region where the solid solution can be formed in a stable state against phase separation; e.g. at 300 K, the alloy cannot be formed in the region of $0.19 < x < 0.68$, which is the miscibility gap. Also, the spinodal and binodal points are found, and thus the alloy can present metastable phases in the intervals of $0.19 < x < 0.28$ and $0.58 < x < 0.68$ at 300 K. Although it is difficult to directly compare these findings with experiment, some indirect experimental evidence such as blue-shift in optical absorption from I-rich to Br-rich compositions were found. For the all-inorganic perovskites such as CsPb$_{(1-x)}$Br$_x$$_3$ [81] and Cs$_8$Rb$_1$$_8$SnI$_{14}$ [82], similar arguments are valid.

4.3. Chemical stability

It is well known that the hybrid halide perovskites are weak on external actions such as humidity, ultraviolet light and heat. Also, whether or not they are stable compounds with respect to chemical decomposition is an important issue. If they are intrinsically stable, the degradation of PSCs can be suppressed by thoroughly protecting the device from the external actions. To check the chemical stability, the following reaction is generally suggested for chemical decomposition of ABX$_3$ perovskites.
Then, the Gibbs free energy difference between the products and the reactants,
\[
\Delta G = G_{\text{ABX}_3} - (G_{\text{BX}_2} + G_{\text{AX}}),
\]
is an estimation of the chemical stability.

Under conditions of zero temperature and zero pressure, simply the DFT total energy difference, i.e. formation energy, can be calculated with this aim [78, 79, 160]. It was found that for MAPI all the possible phases are unstable for chemical decomposition with PBE functional but including the vdW correction gives the orthorhombic phase as stable. As shown in figure 11(a), substituting Cs for MA, Sn for Pb, and Br and Cl for I changes the formation energy from negative to positive, indicating the enhancement of intrinsic chemical stability [160]. Systematic study on mixing I with Br or Cl in MAPI can provide the turning point for the mixing content where the chemical decomposition changes from exothermic to endothermic; 0.2 for MAPb\(_{(I-x)\text{Br}_x}\)\(_3\) [78] and 0.07 for MAPb\(_{(I-x)\text{Cl}_x}\)\(_3\) [79] (figure 11(b)), which agreed well with the experimental findings.

At finite temperature, the vibrational contributions were considered by performing lattice dynamics calculations (mostly via DFPT [85]), revealing that interestingly for MAPI and MASN\(_3\) there is no significant change in Gibbs free energy between the reactant and the products, while for CsSnI\(_3\) its free energy decreases faster than that of CsI and SnI\(_2\). In other work involving MAPI using experimental data for chemical potentials, the free energy difference was calculated to be 0.16 eV \(\text{fu}^{-1}\) at 300 K, indicating that the finite temperature effects tend to stabilize the perovskite structure against spontaneous chemical decomposition under standard thermodynamical conditions [161]. For mixing Cs with Rb in CsPbI\(_3\), the free energy differences tend to increase as the Rb content \(x\) increases, with a turning point. This turning point decreases as the temperature increases, as shown in figure 11(c). The phase diagram for chemical decomposition of CsPbI\(_3\) into PbI\(_2\) and CsI can be obtained as shown in figure 11(d), indicating that CsPbI\(_3\) is stable in the temperature range from 0 to 600 K and in the pressure range from 0 to 4 GPa [149], fitting well with experiment.

5. Defect formation and ion diffusion

As in other well-established semiconductors like Si, the understanding of defects in the halide perovskites is of particular interest to materials engineers as well as scientists who want to improve device performance. In fact, defects in solar cell materials determine a variety of operating processes such as the generation and transport of charge carriers (electrons and holes) and ion diffusion, which are highly important for enhancing the efficiency.
and stability of solar cells. Defects in crystalline solids can be classified into crystallographic defects and
impurities, which are in the form of point defects including vacancies, interstitials, antisites, pair defects
(interstitial and vacancies: Frenkel defect; anion and cation vacancies: Schottky defect), substitutional and
interstitial impurities, or higher-dimensional defects including dislocations, grain boundaries [162] and
precipitates. Such defects can mediate the ion diffusion or can be mobile themselves inside the solid, which is
suggested to be responsible for current–voltage (J–V) hysteresis of a device and degradation related to moisture
and light exposure [163, 164].

Simulations of defect-related phenomena are highly costly from the viewpoint of memory capacity and
computational time. In these simulations, sufficiently large supercells must be adopted to ensure reliable
accuracy of the (charged) defect formation energy, because of the errors caused by the finite sizes of supercells
[165, 166]. To determine the charge transition levels formed by charged defects, the electronic structures of
perfect and defect-containing crystals (modelled by supercells) are calculated with a high accuracy, e.g. using
hybrid functionals such as HSE06 [102] and/or considering SOC effects coupled with many-body theory (GW).
Formation energies of defects depend on the chemical potential of ingredient elements, which are affected by
thermodynamics. The formation enthalpy of a point defect with a charge state \( q \) is calculated using the grand
canonical expression [167–169]

\[
\Delta H_f[D^q] \cong \{ E[D^q] + E_{\text{corr}}[D^q] \} - E_{\text{perf}} - n_i \mu_i + qE_F \tag{17}
\]

where \( E[D^q] \) and \( E_{\text{perf}} \) are the total energies of defect-containing and perfect supercells, \( E_{\text{corr}} \) is the correction
term due to the interaction between the periodic charged defect images, \( E_F \) is the Fermi energy, and \( n_i \) and \( u_i \) are
the number and chemical potential of \( i \)-th species. Every term can be calculated by the first-principles method
coupled with thermodinamics. On the other hand, models and simulations of ion diffusion, which is mostly
vacancy-mediated, need to suggest preliminary migration paths based on the empirical bond valence sum
approach [170], and perform structural optimizations to fix the local configurations and then finally the
minimum energy path calculations using the nudged elastic band (NEB) approach [171] to determine the energy
barrier.

![Figure 11.](image-url)
5.1. Defect formation energy and transition levels
The most important defects in the halide perovskites ABX₃ are the twelve intrinsic point defects: the vacancies (Vₓ, Vᵧ, Vₗ), the interstitials (Aₓ, Bₓ, Xₓ) and the antisites (Aᵧ, Aᵧ, Bᵧ, Bᵧ, Xᵧ, Xᵧ). For each point defect, various charge states are considered. By using equation (17), the formation energies of each point defect with various charge states are calculated as functions of Fermi energy (E₉) at different thermodynamic conditions reflecting the growth conditions. In general, equilibrium conditions for the product with its pure constituents (e.g. MAPI) is in equilibrium with MA, Pb and I₂ give the constraints for the relation between their chemical potentials, resulting in two different scenarios: halide-rich and halide-poor growth conditions. Therefore, two diagrams for defect formation energy can be obtained under these conditions. From these defect formation energy diagrams, it is possible to identify the dominant defect that has the lowest formation energy and thermodynamic charge transition levels.

In the case of tetragonal MAPI, the dominant point defects were found to be the acceptor-type lead vacancy (Vₚb) under I-rich conditions [169, 172, 173], and donor-type MA⁺ under I-poor conditions [172]. Buin et al [174] had slightly different findings, such that the major acceptor defects are Vₚbi, VₘAi and I⁻, whereas the donor defects are Vₗ⁺ and Pb⁻². Among these, defects Vₚbi, MA⁺ and VₘAi were found to possess the lowest formation energies over the entire band gap. The low formation energy of Vₚb is related to the energetically unfavourable s–p antibonding coupling [172]. In the case of MAPbBr₃ and MAPbCl₃ with cubic phases, Pb⁻² has a somewhat comparable formation energy to Vₚb [173, 175]. Interestingly, the dominant defects that have the low formation energies exhibit shallow transition levels in the band gap, while the defects that have higher formation energy (and thus are difficult to form) would have deep-trap levels. In addition, all vacancies yield shallow traps and resonances within the band, implying that charge carriers can still move easily to the VBM and CBM [174]. It has been reported that only interstitial iodine defect Iᵢ is a deep trap and non-radiative recombination centre for holes [176, 177], pointing out the strong dependence of transition levels on the selection of XC functional (HSE + SOC should be used) [178]. Therefore, it can be suggested that point defects in the hybrid halide perovskites should not contribute to the density of deep traps (recombination centres) that directly controls the diffusion length of charge carriers. However, this can be changed according to the growth conditions. For example, the formation energy of deep-level antisite Pbᵢ may be low enough to significantly contribute to the density of recombination centres under I-rich conditions [173, 174]. In this sense, the optimal growth conditions should be halide-poor for MAPI, and halide-rich for MAPbBr₃ and MAPbCl₃ [173].

The experimentally observed unintentional doping for both n-type and p-type MAPI without any added dopant can be explained by the creation of neutral vacancy pair defects, i.e. Schottky defects and Frenkel defects. It was found that Schottky defects such as VPbᵢ and VₘAi, which may dominate defect formation in the halide perovskites under stoichiometric growth conditions, do not make a trap state [179]. The elemental defects derived from Frenkel defects play the role of unintentional doping sources, implying that n-type and p-type doping can be controlled by carefully choosing the proper atomic composition in the growth procedure [180]. Such vacancy pair defects were also considered in the water-intercalated and mono-hydrated MAPI in order to reveal the mechanism of PSC degradation upon exposure to moisture [169]. From the calculated binding energy of the vacancy pair defects, it was concluded that the formation of VPbᵢ from the vacancy point defects Vₗ⁻¹ and Vₚb is spontaneous in these three compounds, while the formation of VₘAi is less favourable than the formation of individual vacancies Vₗ⁻¹ and Vₚb in the hydrous compounds. Moreover, all these Schottky defects exhibit deep-trap levels in the hydrous compounds (figure 12), giving evidence of degradation of PSCs under humid conditions [169].

Defect calculations have been performed for other halide perovskites. By using the GW + SOC method, Li et al [181] investigated the defect physics of cubic CsPbI₃. They found that under Pb-rich conditions the vacancy point defects VPb and Vₗ are the dominant acceptor and donor defects and can pin the Fermi energy in the middle of the band gap due to their comparable formation energies. Under Pb-poor conditions, the acceptor VPb has a high density and thus can generate a high density of hole carriers. While the antisite Pbᵢ acts as the recombination centre under the Pb-rich condition, there are no such centres with a low-energy formation energy under Pb-poor conditions [181]. There exist recent theoretical works on defect physics and chemistry for the hybrid layered perovskite (CH₃NH₃)₂Pb(SCN)₂I₂ [182], the bismuth-based lead-free double perovskites [183], and defect passivation in the hybrid perovskites using quaternary ammonium halide anions and cations [184].

5.2. Ion diffusion
Once the intrinsic ionic defects have formed inside solids, they can migrate according to the minimum energy pathways, as the hybrid perovskites exhibit ionic charge transport as well as electronic conduction in experiments. Such ionic diffusion in the halide perovskites is closely related to the long-term stability and PCE of PSCs. In particular, the anomalous hysteresis of the J–V curves, which is a severe disadvantage of PSCs, and giant switchable PV effects, are importantly invoked by ion migrations [185]. The chemical decomposition of MAPI
upon moisture exposure can also be explained partly by ion diffusion. In simulations, the main tasks are to identify the migrating species and their migration pathways, and to quantitatively determine the underlying energetics, on the condition that the formation of such ionic defects has been already clarified.

Eames et al \[186\] investigated the diffusions of vacancy points (ions), not interstitials, in cubic MAPI, based on the fact that in ABX3 halide perovskites vacancy-mediated ion diffusion is the most acceptable diffusion process while interstitial migration has not been observed in experiments. It should be noted that experiments probing ion migration, however, typically cannot distinguish between different migration pathways. They suggested three vacancy-mediated ion migration pathways including $I^-$ migration along the octahedron edge, Pb$^{2+}$ migration along the diagonal direction and MA$^+$ hopping into a neighbouring vacant site (figure 13(a)).

The activation energies for these ionic migrations were calculated to be 0.58, 2.31 and 0.84 eV\[186\]. When compared with the measured values for hysteresis, the calculated value for $I^-$ is in good agreement with the measured value, 0.60−0.68 eV, whereas for Pb$^{2+}$ and MA$^+$ vacancies they are higher than the measured values, confirming that it is difficult for these ion migrations to occur \[186\]. It should be noted that there is a wide spread of activation energies for ion migrations in both theory and experiments \[187\]. Azpiroz et al \[188\] considered three kinds of vacancy ($V_I$, $V_{PB}$, $V_{MA}$) and the iodine interstitial ($I_i$) in tetragonal MAPI, emphasizing that the migration of MA is responsible for the observed J−V hysteresis. The activation energies of these defects migrations were calculated to be 0.08, 0.46 and 0.80 eV along similar pathways for the three vacancies $V_I$, $V_{MA}$, $V_{PB}$ and 0.08 eV along the c axis for $I_i$. In the case of MAPbBr$_3$, they are 0.09 and 0.56 eV for $V_{PB}$ and $V_{MA}$, respectively. Haruyama et al \[189\] calculated the activation energies as 0.32/0.33 eV for $V_I/V_{PB}$ and 0.57/0.55 eV for $V_{MA}/V_{MA}$ in tetragonal MAPI, 0.55/0.50 eV for $V_I/V_{PB}$ and 0.61/0.57 eV for $V_{FA}/V_{FA}$ in trigonal FAPbI$_3$, and 0.32/0.32 eV for Cl impurity $I_C/I_{CI}$ in cubic MAPbI$_{3−x}Cl_x$. In these calculations, the common conclusion is that halide anions and MA or FA cations are the major ionic carriers due to their relatively low activation energies, which is consistent with the experimental findings and can explain the J−V hysteresis \[190,191\]. Based on the dilute diffusion theory, it was suggested that replacement of MA with the larger cation FA can suppress the hysteresis and prevent ageing in PSC performance \[189\].
Recently, we investigated vacancy-mediated ion migrations in cubic MAPbX$_3$ ($X = I, Br, Cl$), and further water molecular diffusion in their water-intercalated and mono-hydrated phases, aiming to uncover the role of water molecules in the chemical decomposition and thus in the degradation of PSC performance [192]. It was found that the insertion of water into MAPI reduces the activation energies of ion migrations (figure 13(c)), indicating the easy decomposition of the hybrid halide perovskite under humid conditions. Also, the activation barriers for ion and water migrations become higher from $X = I$ to Br to Cl. These results indicate that the decomposition of halide perovskite occurs through a multi-step process such as from water intercalation to hydration and to decomposition, identifying the crucial role of the water molecule in this process. Egger et al [193] investigated hydrogen migration in tetragonal MAPI to explain the hysteresis and material stability. Using the supercells containing a hydrogen impurity with different charge states, they found that the crystal structure may be relaxed significantly for charged hydrogen impurities, collective iodide displacements can enhance proton diffusion, and the migration barriers for proton transfer are relatively low. Based on these findings it was suggested that, in the hybrid halide perovskites, the hydrogen-like defects, introduced either extrinsically or intrinsically, may be mobile and play an important role in explaining the hysteresis effects and stability issues [193].

6. Surface and interface

The device performance and long-term stability of PSCs can be greatly affected by material processes occurring at surfaces, grain boundaries and interfaces. In reality, all bulk materials have a surface due to their finite size, and, as such, the halide perovskite bulk crystals have several types of surfaces classified by hkl-indices and terminations. Moreover, perovskite films are fabricated mostly through solution processing methods, which make them polycrystalline and thus the formation of grain boundaries is unavoidable. With respect to the device structure, it is necessary to adopt electron and/or hole transporting layers that make contact with the photoabsorbing layer, halide perovskite, creating interfaces such as TiO$_2$/MAPI as an interface with the electron
transporting layer. Possibly important material processes at surfaces and interfaces are halide diffusion, ion accumulation, and charge carrier transport and recombination at the defect states. For these phenomena, first-principles modelling and simulations can also provide useful microscopic insights as well.

6.1. Surface phase diagram and electronic states
In the standard simulation techniques using the 3D periodic boundary condition, the surfaces can be modelled by a slab with a supercell, which consists of atomic layers and a vacuum layer. The number of atomic layers and the thickness of the vacuum layer must be checked to ensure that the DFT total energy difference, e.g. the surface formation energy, is not influenced by these modelling parameters. By applying ab initio atomistic thermodynamics, the formation energies of surfaces with various indices and terminations are calculated as functions of chemical potentials of constituent elements at finite temperature and pressure, producing a surface phase diagram.

The structural and electronic properties of tetragonal MAPI surfaces with various indices and terminations have been investigated using DFT calculations with the rev-vdW-DF functional and the inclusion of the SOC effect [194, 195]. Among low-index surfaces considered in that work, tetragonal (110) and (001) surfaces are flat nonpolar surfaces consisting of alternately stacked neutral [MA] and [PbI] planes, while (100) and (101) surfaces are composed of charged [MAPb] and [I] planes, and [MAI] and [PbI] planes, implying large reconstruction or defect formation. Several types of Pb polyhedron terminations were considered but not MA terminations. Identifying the constraint relations between the chemical potentials, the surface phase diagrams were drawn for the four types of surface by calculating the Gibbs free energy differences as functions of the chemical potentials of I and Pb. Through these diagrams, stable terminations in each index surface can be determined for different growth conditions, i.e. Pb-rich (poor) and I-rich (poor) conditions. Also, the relaxed structures and electronic properties were analysed in detail. Based on those calculations, it was concluded that a vacant termination is more stable than the Pb-rich flat termination on all the surfaces under thermodynamic equilibrium growth conditions of bulk MAPI. The flat terminations on the (001) and (110) surfaces were found to have surface states above the bulk valence band (possibly attracting photogenerated holes), which can be efficient intermediates of hole transfer to the adjacent hole transport materials with smaller energy loss [194].

As discussed above, the trapping of charge carriers at defects on the surfaces and grain boundaries is one of the detrimental factors in PSC performance, because it causes nonradiative recombination loss, causes carrier lifetime to deteriorate, and initiates J-V hysteresis. Uratani and Yamashita [196] investigated the types of surface defects responsible for carrier trapping in tetragonal MAPI (001) surfaces by performing HSE + SOC calculations. They constructed (2 × 2) surface models with a vacuum region of 15 Å and three types of termination, i.e. MAI, flat and vacant (figure 14(a)). Several kinds of intrinsic point defect such as vacancies (V), Pb, Pb, and antisites (Pb, Pb) were identified to be formed on each terminated surface, and their formation energies were calculated for I-rich, moderate and Pb-rich conditions. The energy levels of defect states were also drawn in comparison with the VBM and CBM of each system. Using the calculation results, they concluded that under I-rich conditions iodine interstitials I on flat and vacant surfaces are responsible for the carrier trapping, while under Pb-rich conditions V on vacant surfaces and Pb defects are the carrier traps. Therefore, the Pb-rich conditions are better than the I-rich conditions in terms of PV performance, which is consistent with experiments.

Surface modelling and simulations are also important for understanding the interaction of halide perovskites with water, which can be related with the chemical decomposition, especially of MAPI, under humid condition. Such water-assisted chemical decomposition of MAPI can be explained by hydrolysis [60] or hydration [192]. In these processes, the initial step is the adsorption of water on the MAPI surface and its diffusion (or penetration) into the bulk. Liu and co-workers explored the effects of water on the detailed structure and properties of MAPI surfaces based on ab initio MD using the Gaussian-type double-ζ polarized basis sets and the PBE + vdW XC functional [198]. Tetragonal MAPI (001) surfaces with a MA termination were considered as the base surfaces. It was found that the water adsorption energy on the MAPI (001) surface is about 0.30 eV and the diffusion barrier of a water molecule from the surface to the inside region is only about 0.04 eV, indicating that the water can easily penetrate into the bulk. Koocher et al. [197] found that water adsorption is greatly affected by the orientation of the MA cations close to the surface. The activation barriers of water penetrations were calculated to be 0.023 eV in the case of P (the CH, end of the MA molecule towards the top surface) and 0.271 eV in the case of P (the NH, end) on the MAI-terminated (001) surface (figure 14(b)). Therefore, it could be suggested that controlling orientation via poling or interfacial engineering can enhance the moisture stability. Choosing the MAI-terminated (110) surface in MAPI and the MABr-terminated (110) surface in MAPbBr, Zhang et al. [199, 200] calculated the adsorption energies of water molecules to be 1.74 and 1.51 eV with PBE, and 1.87 and 1.67 eV with P + vdW on MAPI and MAPbBr.
surfaces, respectively. They suggested that the deprotonation of the MA cations followed by the desorption of the CH$_3$NH$_2$ molecules is a primary step in the degradation mechanism.

6.2. Interface

In PSCs, the halide perovskite photoabsorbers are sandwiched between the electron transport layer (ETL) and hole transport layer (HTL), so that the photoexcited electrons and holes can be efficiently transported to the collecting electrodes through these layers. In the case of MAPI, for example, it is in contact with a mesoporous TiO$_2$ scaffold as the ETL on one side and with organic Spiro-OMeTAD material as the HTL on other side, thus creating heterojunction interfaces at these contacts [201]. Such interfaces can be considered as large defects, where nonradiative recombination of electrons and holes may occur, resulting in a decrease in PV performance. In fact, charge carrier extraction from the absorber to the transporter can be obstructed at the interfaces by several factors such as interfacial energy barriers originating from imperfect band alignment and charge carrier recombination driven by interfacial defect traps [202]. On the other hand, the interfaces can be weak against the infiltration of external particles such as water molecules and hydrogen atoms or protons, which can trigger or facilitate the degradation of PSCs. Therefore, understanding interface phenomena and further engineering interface structure and composition are very important for improving PSC performance.

---

**Figure 14.** (a) Supercell models of tetragonal MAPI (001) surfaces with MAI, flat PbI$_2$, and vacant PbI$_2$ terminations, displaying cells by dotted lines. Reprinted with permission from [196]. Copyright 2017 American Chemical Society. (b) Lowest-energy structures of water under the first layer of the PbI$_2$-terminated P$^+$ surface (left) and of water initially placed at the hollow site of the PbI$_2$-terminated P$^-$ surface, and the corresponding reaction energy profiles. Reprinted with permission from [197]. Copyright 2015 American Chemical Society.
Mosconi and co-workers investigated the interfaces of TiO₂ to MAPI and also MAPbI₃−ₓClₓ with a small Cl content (~4%) using SOC-DFT calculations [188, 203, 204]. The most stable tetragonal (110) and pseudocubic (001) surfaces of MAPI and MAPbI₃−ₓClₓ were selected and the model systems were made by (3 × 5 × 3) supercells with slab stoichiometries MA₆₀Pb₄₅I₁₅₀ and MA₆₀Pb₄₅I₁₃₅Cl₁₅, which were fully optimized by performing atomic relaxations. These optimized supercells were deposited onto a (5 × 5 × 2) slab of anatase TiO₂ (101) surface made by 120 TiO₂ units. The lattice mismatches were found to be +0.36% and +1.92% for the (110) surfaces, and +0.75% and −1.85% for the (001) surfaces, along the TiO₂ a and b directions, respectively. The binding of perovskite to TiO₂ substrate was found to be through the chemical bond between the perovskite halide atoms and the under-coordinated Ti atoms of the TiO₂ surface. From the simulation results, they conclude that MAPI and MAPbI₃−ₓClₓ tend to grow (110) surfaces on TiO₂ due to their higher binding energies to TiO₂ than (001) surfaces, and interfacial Cl atoms increase the binding energy of the MAPbI₃−ₓClₓ (110) surface compared to MAPI. Through the electronic structure calculations, it was revealed that the interaction of the perovskite with TiO₂ changes the electronic structure strongly to a stronger interfacial coupling between the Ti 3d and Pb 6p conduction band states and to a slight upshift of TiO₂ conduction band energy [203]. In order to investigate the effect of interface defects, vacancies V₁ and V₃MA were created at the perovskite surface exposed to the vacuum (HTL contact) and at the oxide-contacting surface, based on the already established fact that under working conditions V₁ should diffuse towards the HTL and V₃MA towards the ETL side [188]. When compared with the non-defective interface, the outermost valence band states of the perovskite intrude into the band gap of the TiO₂ substrate, while the conduction band states are found inside the manifold of the oxide’s conduction states. The presence of defects at interfaces was found to modify the band alignment, cause the bending of the perovskite bands close to the TiO₂ surface, and create the trap states [188].

For the case of all-inorganic perovskites, the CsPbBr₃/TiO₂ heterostructure has been investigated using the PBEsol+HSE06 functional [205]. From the experimental observations for CsPbBr₃/TiO₂ interfaces, the interface-modified CsBr and PbBr₂ layers were confirmed to have been made during the synthesis, leading to the corresponding CsBr/TiO₂ and PbBr₂/TiO₂ interfaces. From the analysis of the charge population, it was found that large charge transfer occurs between Cs and O atoms, with much smaller charge transfer between Br and Ti atoms, being caused by the interface effects. Accordingly, the charge difference was plotted before and after the interface formation: charge accumulation occurs on Ti and O atoms, but depletion on Cs and Br atoms, implying electron transfer from the perovskite to the TiO₂. From the integrated local DOS projected along the direction perpendicular to the interface, the staggered gap offset junction was observed for both interfaces, revealing the driving force of the charge transfer through the interfaces. Moreover, the band gap in the regions far away from the interface is almost consistent with that of individual CsPbBr₃ or TiO₂, whereas in the vicinity of the interface it decreases. The interface electronic states were found to be located on the conduction band edge of CsPbBr₃, indicating the shallow gap states. It was suggested that these shallow gap states may increase the absorbed photons and promote optical absorption [205].

Regarding the degradation issue, the interaction between the MAPI surface and a liquid water environment was investigated by making a slab interface model consisting of MAPI surface and water molecules and performing ab initio MD simulations [206]. The perovskite surfaces were made by cutting (2 × 2) slabs from the bulk tetragonal MAPI crystal, leading to (001) surfaces with three kinds of termination: MAI, PbI₂ and PbI₂-defective terminations. To generate the defective surface, six PbI₂ units were removed out of a total of eight PbI₂ units from the PbI₂-terminated (001) surface [194]. The vacancy region was filled with water molecules, the numbers of which were determined from the experimental density of liquid water as 284, 226 and 235 for MAI-terminated, PbI₂-terminated and PbI₂-defective surfaces, respectively. By analysing the MD trajectories, the MAI-terminated slabs were found to undergo rapid solvation according to a nucleophilic substitution of I by water, desorption of MA molecules, and thus net dissolution of a MAI molecule. In contrast, the PbI₂-terminated surfaces were stable against such a solvation process, although the percolation of a water molecule can occur to form a hydrated bulk phase. It was also concluded that PbI₂ defects may facilitate the solvation of the surface and initiate the degradation of the entire perovskite.

7. Summary and outlook

Being inspired by the astonishing experimental findings for PSCs, a lot of computational works on the halide perovskites have been carried out within the latest five years in order to reveal the underlying mechanisms of perovskites’ physics and chemistry and indicate ways to find new perovskites with improved performance. In this review, we have presented a critical discussion about the theoretical findings and conclusions for crystalline structures, electronic and optical properties, lattice dynamics and material stabilities, defect physics and ionic diffusions, and surfaces and interfaces in the hybrid organic–inorganic and purely all-inorganic halide perovskites, which have been made based on first-principles calculations. Specific theories, methods, and
modelling approaches for these calculations have been provided, trying to point out the discrepancy and limit of the modelling and calculations when compared with the available experimental data. Special attention has been paid to making clear the structure–property relationships in these materials, which were closely associated with PV performance (efficiency and stability). We have demonstrated the predicting power of first-principles materials design with some predictions for new halide perovskites unexplored by experiment or optimal mixing ratios in some solid solutions.

In order to commercialize PSCs to make an impact on global energy market share, the efficiency and stability of PSCs need to be further improved, as efficiency is still under the maximum theoretical efficiency of 25% ~ 27% estimated by first-principles modelling [207]. In particular, the inherent chemical instability of halide perovskites under working conditions such as a humid, light and thermal environment should be of primary urgency in commercialization. On the one hand, performance enhancement can be realized by identifying the most ideal device architecture, as some material–architecture combinations have shown high efficiency and stability. On the other hand, due to the rich versatility of halide perovskites with respect to chemical composition and structural phase, it is desirable to find the optimal choices of composition and structure that can give the best performance of a PSC. Relying on computational or coupled experimental–computational methods will be the best way to achieve this aim with respect to the time and cost involved.

Band gap engineering is the first thing to do. Once the chemical composition and crystalline structure are identified, the band gap can be calculated in an almost autonomous way with tolerable time and computational demands. However, much more time-consuming methods beyond standard DFT, such as hybrid functional and GW, could be needed to get a reliable band gap, and especially band alignment. Then, lattice dynamics should be performed to estimate the material stability at finite temperature and pressure. Although quasi-harmonic approximation can be used to obtain phonon dispersion, anharmonicity that the perovskites exhibit inherently should be considered; this is not yet well-established. Anharmonicity in lattice dynamics could be related to the ferroelectric nature of perovskite, which is still in debate. To save time and cost, inexpensive interatomic potential functions can be used in lattice dynamics but with careful consideration of accuracy. Finally, defect and interface engineering are also of great importance in determining the direct relation between synthesis processes and device architecture. Despite progress in these respects, many important questions remain untouched, e.g. proton percolation into the interface and influence on performance.

Acknowledgments

I am profoundly grateful to Professor Aron Walsh and Professor C Richard A Catlow for their kind invitation to the Thomas Yang Centre 5th Energy Workshop held in London, useful discussions during my stay there, and the positive recommendation for writing this topical review. This work was partly supported by the State Committee of Science and Technology, Democratic People’s Republic of Korea, under the fundamental research project ‘Design of Innovative Functional Materials for Energy and Environmental Application’ (No. 2016–20).

Notes

The author declares no competing financial interest.

ORCID iDs

Chol-Jun Yu @ https://orcid.org/0000-0001-9523-4325

References

[1] European Commission Climate Action 2015 Annual Conference of Parties (COP) at COP21 at Stade de France (Gate E) in Paris (http://ec.europa.eu/clima/policies/international/negotiations/paris/index_en.htm)
[2] Catlow C R A, Guo Z X, Miskufova M, Shevlin S A, Smith A G H, Sokol A A, Walsh A, Wilson D J and Woodley S M 2010 Advances in computational studies of energy materials Phil. Trans. R. Soc. A 368 3379–456
[3] Chu S, Cui Y and Liu N 2017 The path towards sustainable energy Nat. Mater. 16 16–22
[4] Green M A, Emery K, Hishikawa Y, Warta W, Dunlop E D, Levi D H and Ho-Baillie A W Y 2017 Solar cell efficiency tables (version 49) Prog. Photovolt., Res. Appi. 25 3–13
[5] Kojima A, Teshima K, Shirai Y and Miyasaka T 2009 Organometal halide perovskites as visible-light sensitizers for photovoltaic cells J. Am. Chem. Soc. 131 6050–1
[6] Im J H, Lee C R, Lee J W, Park S W and Park N-G 2011 6.5% efficient perovskite quantum-dot-sensitized by lead-halide compounds Nanoscale 3 4088–93
[7] Lee M M, Teuscher J, Miyasaka T, Murakami T N and Snaith H J 2012 Efficient hybrid solar cells based on meso-superstructured organometal halide perovskite Science 338 643–7
[8] Kim H S et al 2012 Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9% Sci. Rep. 2 591
[9] Burschka J, Pellet N, Moon S J, Humphry-Baker R, Gao P, Nazareuddin M K and Grätzel M 2013 Sequential deposition as a route to high-performance perovskite-sensitized solar cells Nature 499 316–9
[10] Zhou H, Chen Q, Li G, Luo S, Song T-B, Duan H-S, Hong Z, You J, Liu Y and Yang Y 2014 Interface engineering of highly efficient perovskite solar cells Science 345 542–6
[11] Jeon N J, Noh J H, Yang W S, Kim Y C, Ryu S, Seo J and Seok S J 2015 Compositional engineering of perovskite materials for high-performance solar cells Nature 517 476–80
[12] Yang W S et al 2017 Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells Science 356 1376–9
[13] Snaith H J 2013 Perovskites: the emergence of a new era for low-cost, high-efficiency solar cells J. Phys. Chem. Lett. 4 3623–30
[14] Park N-G 2013 Organometal perovskite light absorbers toward a 20% efficiency low-cost solid-state mesoscopic solar cell J. Phys. Chem. Lett. 4 2423–32
[15] Li Y, J H, Liu R, Zhang C, Mak H C, Zou X, Shen H H, Leu S-Y and Hsu H-Y 2018 A review on morphology engineering for highly efficient and stable hybrid perovskite solar cells J. Mater. Chem. A 6 12842–75
[16] Chen X, Lu H, Yang Y and Beard M C 2018 Excitonic effects in methylammonium lead halide perovskites J. Phys. Chem. Lett. 9 2593–603
[17] Huang J, Yuan Y, Shao Y and Yan Y 2017 Understanding the physical properties of hybrid perovskites for photovoltaic applications Nat. Rev. Mater. 2 17042
[18] Ibn-Mohammed T, Koh S C L, Reaney I M, Acquaye A, Schileo G, Mustapha K B and Greenough R 2017 Perovskite solar cells: an integrated lifecycle assessment and review in comparison with other photovoltaic technologies Renew. Sust. Energy Rev. 80 1321–44
[19] Mahmood K, Sarwar S and Mehran M T 2017 Current status of electron transport layers in perovskite solar cell materials: and properties RSC Adv. 7 10744–62
[20] Hoye R L Z et al 2017 Perovskite-inspired photovoltaic materials: toward best practices in materials characterization and calculations Chem. Mater. 29 1964–88
[21] Xiao Z, Yuan Y, Wang Q, Shao Y, Bai Y, Deng Y, Dong Q, Hu M, Bi C and Huang J 2016 Thin-film semiconductor perspective of organometal trihalide perovskite materials for high-efficiency solar cells Mater. Sci. Eng. R 101 1–38
[22] Park N-G, Grätzel M, Miyasaka T, Zhu K and Emery K 2016 Towards stable and commercially available perovskite solar cells Nat. Energy 1 16152
[23] Zuo C, Bolink H J, Han H, Huang J, Cahen D and Ding L 2016 Advances in perovskite solar cells Adv. Sci. 3 1500324
[24] Sum T C and Mathews N 2014 Advancements in perovskite solar cells: photosynthesis behind the photovoltaics Energy Environ. Sci. 7 2518–34
[25] Wang D, Wright M, Elumalai N K and Uddin A 2016 Stability of perovskite solar cells Sol. Energy Mater. Sol. Cells 147 235–55
[26] Berhe T A, Su W-N, Chen C-H, Pan C-J, Cheng J-H, Chen H-M, Tsai M-C, Chen L-Y, Dubale A A and Hwang B-J 2016 Organometal halide perovskite solar cells: degradation and stability Energy Environ. Sci. 9 523–56
[27] Li B, Li Y, Zheng C, Gao D and Huang W 2016 Advancements in the stability of perovskite solar cells: degradation mechanisms and improvement approaches RSC Adv. 6 38079–91
[28] Niu G D, Guo X D and Wang L D 2013 Review of recent progress in chemical stability of perovskite solar cells J. Mater. Chem. A 3 8970–80
[29] Manser J S, Saidaminov M I, Christians J A, Baker O M and Kamat P V 2016 Making and breaking of lead halide perovskites Acc. Chem. Res. 49 330–8
[30] Li Z, Klein T R, Kim D H, Yang M, Berry J J, van Hest M F A M and Zhu K 2018 Scalable fabrication of perovskite solar cells Nat. Rev. Mater. 3 18017
[31] Chatterjee S and Pal A J 2018 Influence of metal substitution on hybrid halide perovskites: towards lead-free perovskite solar cells J. Mater. Chem. A 6 3793–822
[32] Butler K T, Frost J M, Skelton J M, Svanæ K L and Walsh A 2016 Computational materials design of crystalline solids Chem. Soc. Rev. 45 6138–46
[33] Luo S and Daoud W A 2015 Recent progress in organic–inorganic halide perovskite solar cells: mechanisms and materials design J. Mater. Chem. A 3 8992–9010
[34] Walsh A 2015 Principles of chemical bonding and band gap engineering in hybrid organic–inorganic halide perovskite J. Phys. Chem. C 119 5753–60
[35] Frost J M and Walsh A 2016 What is moving in hybrid halide perovskite solar cells? Acc. Chem. Res. 49 528–35
[36] Butler K T, Walsh A, Cheetham A K and Kieslich G 2016 Organised chaos: entropy in hybrid inorganic–organic systems and other materials Chem. Sci. 7 6316–24
[37] Whalley L D, Frost J M, Jung Y-K and Walsh A 2017 Perspective: theory and simulation of hybrid halide perovskites J. Chem. Phys. 146 220901
[38] Mattoni A, Filippetti A and Caddeo C 2016 Modelling hybrid perovskites by molecular dynamics J. Phys.: Condens. Matter 29 43001
[39] Yin W-J, Yang J-H, Kang J, Yan Y and Wei S-H 2015 Halide perovskite materials for solar cells: a theoretical review J. Mater. Chem. A 3 8926–42
[40] Manser J S, Christians J A and Kamat P V 2016 Intriguing optoelectronic properties of metal halide perovskites Chem. Rev. 116 12956–3008
[41] Hautier G, Miglio A, Ceder G, Rignanese G-M and Gonze X 2013 Identification and design principles of low hole effective mass p-type transparent conducting oxides Nat. Commun. 4 2292
[42] Isayev O, Fournches D, Muratov E N, Oses C, Rasch K, Tropsa A and Curtarolo S 2015 Materials cartography: representing and mining materials space using structural and electronic fingerprints Chem. Mater. 27 735–43
[43] Oganov A R, Lyakhov A O and Valle M 2011 How evolutionary crystal structure prediction works—and why Acc. Chem. Res. 44 227–37
[44] Pickard C J and Needs R J 2011 J. Phys.: Condens. Matter 23 053201
[45] Goldschmidt V M 1926 Die gesetze der kry stallochemie Naturwissenschaften 14 477–85
[46] Stoumpos C C and Kanatzidis M G 2015 The renaissance of halide perovskites and their evolution as emerging semiconductors Acc. Chem. Res. 48 2791–802

[47] Travis W, Glover E N K, Bronstein H, Scanlon D O and Palgrave R G 2016 On the application of the tolerance factor to inorganic and hybrid halide perovskites: a revised system Chem. Sci. 7 4548–56

[48] Kieslich G, Sun S and Cheetham A K 2015 An extended tolerance factor approach for organic–inorganic perovskites Chem. Sci. 6 3430–3

[49] Li C, Lu X, Ding W, Feng L, Gao Y and Guo Z 2008 Formability of ABX3 (X = F, Cl, Br, I) halide perovskites Acta Crystallogr. B 64 702–7

[50] Shannon R D 1976 Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides Acta Crystallogr. A 32 751–67

[51] Lide D R 2004 CRC Handbook of Chemistry and Physics (Boca Raton, FL: CRC Press)

[52] Beecher A N, Semontin O E, Skelton J M, Frost J M, Terban M W, Zhai H, Alatas A, Owen J S, Walsh A and Billing J S L 2016 Direct observation of dynamic symmetry breaking above room temperature in methylammonium lead iodide perovskite ACS Energy Lett. 1 880–7

[53] Legay A M A et al 2015 The dynamics of methylammonium ions in hybrid organic–inorganic perovskite solar cells Nat. Commun. 6 7124

[54] Glazer A M 1972 The classification of tilted octahedra in perovskites Acta Crystallogr. B 28 3384–92

[55] Pogliotti A and Weber D 1987 Dynamic disorder in methylammoniumtrihalogenoplumbates (ii) observed by millimeter-wave spectroscopy J. Chem. Phys. 87 6383–3788

[56] Brivio F, Walker A B and Walsh A 2013 Structural and electronic properties of hybrid perovskites for high-efficiency thin-film photovoltaics from first-principles Appl. Mater. 10 42111

[57] Yu C-J, Jong U-G, Ri M-H, Ri G-C and Pae Y-H 2016 Electronic structure and photoabsorption property of pseudo-cubic perovskite CH3NH3PbX3 (X = I, Br) including van der Waals interaction J. Mater. Sci. 51 9849–54

[58] Mosconi E, Quarti C, Ivanovska T, Ruani G and De Angelis F 2014 Structural and electronic properties of organo-halide lead perovskites: a combined IR spectroscopy and ab initio molecular dynamics investigation Phys. Chem. Chem. Phys. 16 16131–44

[59] Frost J M, Butler K T and Walsh A 2014 Molecular ferrocene contributions to anomalous hysteresis in hybrid perovskite solar cells Appl. Mater. 2 081506

[60] Frost J M, Butler K T, Brivio F, Hendon C H, van Schilfgaarde M and Walsh A 2014 Atomistic origins of high-performance in hybrid halide perovskite solar cells Nano Lett. 14 2584–90

[61] Geng W, Zhang L, Zhang Y-N, Lai W-M and Liu L-M 2014 First-principles study of lead iodide perovskite tetragonal and orthorhombic phases for photovoltaics J. Phys. Chem. C 118 19565–71

[62] Yang R X, Skelton J M, Lora da Silva E, Frost J M and Walsh A 2017 Spontaneous octahedral tilting in the cubic inorganic cesium halide perovskites CsSnX3 and CsPbX3 (X = F, Cl, Br, I) J. Phys. Chem. Lett. 8 4720–6

[63] Yamada K, Funabiki S, Horimoto H, Matsui T, Okuda T and Ichiba S 1991 Structural phase transitions of the polymorphs of CsSnI3 Phys. Rev. B 44 10579–82

[64] Savory C N, Walsh A and Scanlon D O 2018 Pb-free hybrid perovskites support high-efficiency solar cells APL Mater. 6 246102

[65] McClure E T, Ball M R, Windl W and Woodward P M 2016 Cs2AgBiX6 (X = Br, I) synthesized by Cs cation-exchange on inorganic Sn halide perovskites J. Mater. Sci. 51 1254–57

[66] Meng W, Wang W, Wang J, Mitzi D B and Yan Y F 2017 Searching for promising new perovskite-based photovoltaic absorbers: the importance of electronic dimensionality Mater. Horiz. 4 206–16

[67] Savory C N, Walsh A and Scanlon D O 2016 Can Pb-free halide double perovskites support high-efficiency solar cells? ACS Energy Lett. 1 494–503

[68] Wei F, Deng Z, Sun S, Zhang L, Visitors F, Evans D M, Carpenter M A, Bristowe P D and Cheetham A K 2016 The synthesis, structure and electronic properties of a lead-free hybrid–organic–inorganic double perovskite (MA)2KBr6 (MA = methylammonium) Mater. Horiz. 3 2520–6

[69] Lora da Silva E, Skelton J M, Parker S C and Walsh A 2015 Phase stability and transformations in the halide perovskite CsSnI3 J. Phys. Rev. B 91 144107

[70] Yan J, Qiu W, Wu G, Heremans L and Lora da Silva E, Frost J M and Walsh A 2017 Recent progress in 2D/quasi-2D layered metal halide perovskites for solar cells J. Mater. Chem. A 5 11063–77

[71] Maughan A E, Gannaway A M, Almaker M A, Scanlon D O and Neilson J R 2018 Tolerance factor and cooperative tilting effects in vacancy-ordered double perovskite halides Chem. Mater. 30 3909–19

[72] Xiao Z W, Meng W W, Wang J B, Mitzi D B and Yan Y F 2017 Searching for promising new perovskite-based photovoltaic absorbers: the importance of electronic dimensionality Mater. Horiz. 4 206–16

[73] Savory C N, Walsh A and Scanlon D O 2016 Can Pb-free halide double perovskites support high-efficiency solar cells? ACS Energy Lett. 1 494–503

[74] McClure E T, Ball M R, Windl W and Woodward P M 2016 Cs2AgBiX6 (X = Br, Cl): new visible light absorbing, lead-free halide perovskite semiconductors Chem. Mater. 28 1348–54

[75] Wei F, Deng Z, Sun S, Xie F, Kieslich G, Evans D M, Carpenter M A, Bristowe P D and Cheetham A K 2016 The synthesis, structure and electronic properties of a lead-free hybrid–organic–inorganic double perovskite (MA)2KBr6 (MA = methylammonium) Mater. Horiz. 3 2520–6

[76] Deng Z, Wei F, Sun S, Kieslich G, Cheetham A K and Bristowe P D 2016 Exploring the properties of lead-free hybrid double perovskites using a combined computational–experimental approach J. Mater. Chem. A 4 12025–9

[77] Filip M R, Hillman S, Haghighirad A A, Snaith H J and Giustino F 2016 Band gaps of the lead-free halide double perovskites Cs2BAgBr6 and Cs2BAgI6 from theory and experiment J. Phys. Chem. Lett. 7 2379–85

[78] Volonakis G, Filip M R, Haghighirad A A, Sakai N, Wengar S, Snaith H J and Giustino F 2016 Lead-free halide double perovskites via heterovalent substitution of noble metals J. Phys. Chem. Lett. 7 12549–54

[79] Ono L K, Juarez-Perez E J and Qi Y 2017 Progress on perovskite materials and solar cells with mixed cations and halide anions ACS Appl. Mater. Interfaces 9 30197–246

[80] Brivio F, Caetano C and Walsh A 2016 Thermodynamic origin of photostability in the CH3NH3PbI3 (x = 0) hybrid halide perovskite J. Phys. Chem. Lett. 7 1083–7

[81] mosconi e, amat a, nazeeruddin m k, graitzel m and de angelis f 2013 First-principles modeling of mixed halide organometal perovskites for photovoltaic applications J. Phys. Chem. C 117 13902–13

[82] Jong U-G, Yu C-J, Kir I-S, Kim N-H and Ri G-C 2016 Influence of halide composition on the structural, electronic, and optical properties of mixed CH3NH3PbI3 (x = 0) perovskites calculated using the virtual crystal approximation method Phys. Rev. B 94 125139

[83] Jong U-G, Yu C-J, Jung Y-M, Ri G-C, Hong S-N and Pae Y-H 2017 Revealing the stability and efficiency enhancement in mixed halide perovskites MAPbI3 (x = 0.05) with ab initio calculations J. Power Sources 350 65–72

[84] Saitdaminov M I et al 2018 Isovalent small ions suppress atomic vacancies in perovskites Nat. Energy 3 648–54

[85] Yin W-J, Yan Y and Wei S-H 2014 Anomalous alloy properties in mixed halide perovskites J. Phys. Chem. Lett. 5 3625–31

[86] Jung Y-K, Lee J-H, Walsh A and Soon A 2017 Influence of Rb/Cs cation-exchange on inorganic Sn halide perovskites: from chemical structure to physical properties Chem. Mater. 29 3181–8
[158] Grau-Crespo R, Hamad S, Calow C R A and de Leeuw H N H 2007 Symmetry-adapted configurational modelling of fractional site occupancy in solids J. Phys.: Condens. Matter 19 256201
[159] Sher A, van Schilfgaarde M, Chen A-B and Chen W 1987 Quasichemical approximation in binary alloys Phys. Rev. B 36 4279
[160] Zhang Y-Y, Chen S, Xu P, Xiang H, Gong X-G, Walsh A and Wei S-H 2018 Intrinsic instability of the hybrid halide perovskite semiconductor CH$_3$NH$_3$PbI$_3$ Chin. Phys. Lett. 35 036104
[161] Tenuta E, Zheng C and Rubel O 2016 Thermodynamic origin of instability in hybrid halide perovskites Sci. Rep. 6 37654
[162] Long R, Liu J and Prezhdo O V 2016 Unravelling the effects of grain boundary and chemical doping on electron–hole recombination in CH$_3$NH$_3$PbI$_3$ perovskite by time-domain atomic simulation J. Am. Chem. Soc. 138 3884–90
[163] Walsh A and Zunger A 2017 Instilling defect tolerance in new compounds Nat. Mater. 16 964–7
[164] Ball M and Petrozza A 2016 Defects in perovskite–halides and their effects in solar cells Nat. Energy 1 149
[165] Kumagai Y and Oba F 2014 Electrostatics-based finite-size corrections for first-principles point defect calculations Phys. Rev. B 89 195205
[166] Kumagai Y, Burton I, Walsh A and Oba F 2016 Electronic structure and defect physics of in sulfides: SnS$_2$, SnSe$_2$, and SnS$_2$ Phys. Rev. Appl. 6 014005
[167] Zhang S B and Northrup I E 1991 Chemical potential dependence of defect formation energies in GaAs application to Ga self-diffusion Phys. Rev. Lett. 67 2399
[168] Freysoldt C, Grabowski B, Hickel T, Neugebauer J, Kresse G, Janotti A and Van de Walle C G 2014 First-principles calculations for point defects in solids Rev. Mod. Phys. 86 253–305
[169] Kye Y-H, Yu C-J, Jong U-G, Chen Y and Walsh A 2018 Critical role of water in defect chemistry and chemical degradation of perovskite solar cells J. Phys. Chem. Lett. 9 2196–201
[170] Brown I D and Altermatt D 1985 Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database Acta Crystallogr. B 41 244–7
[171] Henkelman G, Uberuaga B P and Jonsson H 2000 A climbing image nudged elastic band method for finding saddle points and minimum energy paths J. Chem. Phys. 113 9901–4
[172] Yin W-J, Shi T and Yan Y 2014 Unusual defect physics in CH$_3$NH$_3$PbI$_3$ perovskite solar cell absorber Appl. Phys. Lett. 104 063903
[173] Buin A, Comin R, Xu J, Ip A H and Sargent E H 2015 Halide–dependent electronic structure of organolead perovskite materials Chem. Mater. 27 4405
[174] Buin A, Pietsch P, Xu J, Voznyy O, Ip A H, Comin R and Sargent E H 2014 Materials processing routes to trap-free halide perovskites Nano Lett. 14 6281–6
[175] Shi T, Yin W-J, Hong F, Zhu K and Yan Y 2015 Unipolar self-doping behavior in perovskite CH$_3$NH$_3$PbBr$_3$ Appl. Phys. Lett. 106 103902
[176] Du M H 2014 Efficient carrier transport in halide perovskites: theoretical perspectives J. Mater. Chem. A 2 9091–8
[177] Li W, Liu J, Bai F-Q, Zhang H-X and Prezhdo O V 2017 Hole trapping by iodine interstitial defects decreases free carrier losses in perovskite solar cells: a time-domain ab initio study ACS Energy Lett. 2 1270–8
[178] Du, Density M-H 2015 Functional calculations of native defects in CH$_3$NH$_3$PbI$_3$: effects of spin–orbit coupling and self-interaction error J. Phys. Chem. Lett. 6 1461–6
[179] Walsh A, Scanlon D O, Chen S, Gong X and Wei S-H 2015 Self-regulation mechanism for charged point defects in hybrid halide perovskites Angew. Chem., Int. Ed. 54 17194–91
[180] Kim J, Lee S-H, Lee J H and Hong K-H 2014 The role of intrinsic defects in methylammonium lead iodide perovskite J. Phys. Chem. Lett. 5 1317–2
[181] Li Y, Zhang C, Zhang X, Huang D, Shen Q, Cheng Y and Huang W 2017 Intrinsic point defects in inorganic perovskite CaPbI$_3$ from first-principles prediction Appl. Phys. Lett. 111 162106
[182] Ganose A M, Savory C N and Scanlon D O 2017 Electronic and defect properties of (CH$_3$NH$_3$)$_2$Pb(SCN)$_2$I$_4$ analogues for photovoltaic applications J. Mater. Chem. A 5 7845–53
[183] Xiao Z, Meng W, Wang J and Yan Y 2016 Thermodynamic stability and defect chemistry of bismuth–based lead-free double perovskites ChemSusChem 9 2628–33
[184] Zheng X, Chen B, Dai J, Fang Y, Bai Y, Lin Y, Wei H, Zeng X-C and Huang J 2017 Defect passivation in hybrid perovskite solar cells using quaternary ammonium halide anions and cations Nat. Energy 2 17102
[185] Richardson G, O’Kane S E J, Niemann R G, Peltola T A, Foster J M, Cameron P J and Walker A B 2016 Can slow-moving ions explain hysteresis in the current–voltage curves of perovskite solar cells? Energy Environ. Sci. 9 1476–85
[186] Eames C, Frost J M, Barnes P R F, O’Regan B C, Walsh A and Islam M S 2015 Ionic transport in hybrid lead iodide perovskite solar cells Nat. Commun. 6 7497
[187] Li C, Guerrero A, Zhong Y and Huettner S 2017 Origins and mechanisms of hysteresis in organometal halide perovskites J. Phys.: Condens. Matter 29 193001
[188] Aeppli J M, Mosconi E, Bisquert J and De Angelis F 2015 Defects migration in methylammonium lead iodide and their role in perovskite solar cells operation Energy Environ. Sci. 8 2518–27
[189] Haruyama J, Sodeyama K, Han L and Tateyama Y 2015 First-principles study of ion diffusion in perovskite solar cell sensitizers J. Am. Chem. Soc. 137 10048–51
[190] Yuan Y, Wang Q, Shao Y, Lu H, Li T, Gruevman A and Huang J 2016 Electric-field-driven reversible conversion between methylammonium lead triiodide perovskites and lead iodide at elevated temperatures Adv. Energy Mater. 6 1501803
[191] Yuan Y, Chae J, Shao Y, Wang Q, Xiao Z, Centrone A and Huang J 2015 Photovoltaic switching mechanism in layered structure hybrid perovskite solar cells Adv. Energy Mater. 5 1500615
[192] Jong U-G, Yu C-J, Ri G-C, McMahon A P, Harrison N M, Barnes P R F and Walsh A 2018 Influence of water intercalation and hydration on chemical decomposition and ion transport in methylammonium lead halide perovskites J. Mater. Chem. A 6 1067–74
[193] Eger D A, Kronik L and Rappe A M 2013 Theory of hydrogen migration in organic–inorganic halide perovskites Acc. Chem. Res. 46 554–61
[194] Haruyama J, Sodeyama K, Han L and Tateyama Y 2014 Termination dependence of tetragonal CH$_3$NH$_3$PbI$_3$ surfaces for perovskite solar cells J. Phys. Chem. Lett. 5 2903–9
[195] Haruyama J, Sodeyama K, Han L and Tateyama Y 2016 Surface properties of CH$_3$NH$_3$PbI$_3$ for perovskite solar cells Acc. Chem. Res. 49 554–61
[196] Uratani H and Yamashita K 2017 Charge carrier trapping at surface defects of perovskite solar cell absorbers: a first-principles study J. Phys. Chem. Lett. 8 742–6
[197] Koocher N Z, Saldana-Greco D, Wang F, Liu S and Rappe A M 2015 Polarization dependence of water adsorption to CH$_3$NH$_3$PbI$_3$ (001) surfaces J. Phys. Chem. Lett. 6 4371–8

[198] Tong C-J, Geng W, Tang Z-K, Yam C-Y, Fan X-L, Liu J, Lau W-M and Liu L-M 2015 Uncovering the veil of the degradation in perovskite CH$_3$NH$_3$PbI$_3$ upon humidity exposure: a first-principles study J. Phys. Chem. Lett. 6 3289–95

[199] Zhang L and Sit P H-L 2015 Ab initio study of interaction of water, hydroxyl radicals, and hydroxide ions with CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$ surfaces J. Phys. Chem. C. 119 22370–8

[200] Zhang L, Liu X, Su J and Li J 2016 First principles study of molecular adsorption on lead iodide perovskite surface: a case study of halogen bond passivation for solar cell application J. Phys. Chem. C 120 23536–41

[201] Butler K T, Kumagai Y, Oba F and Walsh A 2016 Screening procedure for structurally and electronically matched contact layers for high-performance solar cells: hybrid perovskites J. Mater. Chem. C 4 1149–58

[202] Schulz P 2018 Interface design for metal halide perovskite solar cells ACS Energy Lett. 3 1287–93

[203] Mosconi E, Ronca E and De Angelis F 2014 First-principles investigation of the TiO$_2$/organohalide perovskites interface: the role of interfacial chlorine J. Phys. Chem. Lett. 5 2619–25

[204] Roiati V, Mosconi E, Listorti A, Colella S, Gigli G and De Angelis F 2014 Stark effect in perovskite/TiO$_2$ solar cells: evidence of local interfacial order Nano Lett. 14 2168–74

[205] Qian C-X, Deng Z-Y, Yang K, Feng J, Wang M-Z, Yang Z, Liu S and Feng H-J 2018 Interface engineering of CaPbBr$_2$/TiO$_2$ heterostructure with enhanced optoelectronic properties for all-inorganic perovskite solar cells Appl. Phys. Lett. 112 093901

[206] Mosconi E, Azpiroz J M and De Angelis F 2015 Ab initio molecular dynamics simulations of methylammonium lead iodide perovskite degradation by water Chem. Mater. 27 4885–92

[207] Gränäs O, Vinichenko D and Kaxiras E 2016 Establishing the limits of efficiency of perovskite solar cells from first principles modeling Sci. Rep. 6 36108