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Defects and Their Passivation in Hybrid Halide Perovskites toward Solar Cell Applications

Abhishek Maiti, Soumyo Chatterjee, Lekha Peedikakkandy, and Amlan J. Pal*

The rise of hybrid metal-halide perovskites as potential solar energy materials has revolutionized research on next-generation solar cells. According to recent studies, the rationale behind such success is the rich defect physics of materials. Studies on the origin of different types of prevailing defects, their formation, and mechanism of defect passivation have hence become decisive avenues. Herein, the possible origins of defects and different defect analysis techniques in hybrid halide perovskites are discussed. While initiating the discussion with the archetypal methylammonium lead halide, perovskites beyond the conventional ABX₃ structure are included. In this direction, some major advancements to date on defect formation in the bulk of hybrid halide perovskites, at the grains and grain boundaries, are summarized. Numerous effective methods to passivate the defects and the adverse effect of defects on device efficiency are further highlighted. Hence, the prospect of defect engineering in perovskite materials is pointed toward improving the power conversion efficiency and long-term stability of perovskite solar cells (PSCs). The discussion rightfully addresses that the in-depth exploration of defect engineering is anticipated to have a gigantic impact toward the achievement of predicted efficiency in metal-halide PSCs.

1. Introduction

In the present decade, researchers have witnessed an unprecedented success in the arena of materials for solar cells through the introduction of hybrid halide perovskites.^[1–5] An amazing rise in the power conversion efficiency (PCE) of such perovskite solar cells (PSCs) along with their low fabrication cost has made this class of materials a viable alternative to silicon for commercialization.^[4,6,7] The most investigated member of this perovskite family is methylammonium lead iodide (CH₃NH₃PbI₃ aka MAPbI₃ aka MAPI) which carries the well-known structural formula of ABX₃. Here, the A-site is usually occupied by an organic or inorganic monovalent cation, the B-site by a divalent lead cation, and the X-site by a halogen.^[1,8,9] The unprecedented success of MAPbI₃ in solar cell applications is due to a plethora of optimal properties, such as a tunable and appropriate optical bandgap,^[10–12] a high absorption coefficient,^[13,14] a high carrier

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mobility,^[15] a long carrier diffusion length,^[16] an extraordinarily high defect tolerance,^[17] and a low recombination loss,^[18,19] which have propelled the PCE of solar cells based on the material to reach a record breaking value of 25.2% to date at the lab scale.^[20] Although a large number of noteworthy developments have taken place in the research field of hybrid halide perovskites since its inception, the material still possesses a couple of major limitations, namely toxicity of lead and long-term ambient stability.^[21,22] To address these inadequacies, contemporary researches expectedly focused mostly on materials engineering in CH₃NH₃PbI₃; in this direction, the substitution of lead by a suitable metal and use of a bulky organic cation at the A-site have shown further promises.^[23,24] As a consequence, the prototype perovskite, CH₃NH₃PbI₃, has now become the representative of a large family of analogous compounds appropriate for efficient solar cell applications.

Besides remarkable advances related to materials engineering in the perovskite, defect physics, being a fundamental issue in device research, has also shared the spotlight significantly over the past few years.^[25,26] As such, the polycrystalline nature of hybrid halide perovskite materials has made them prone to defects which inevitably put a roadblock toward the improvement of device efficiency.^[27–29] In solar cell architectures, these defects act as recombination centers in the bulk of the material; in addition, grains and grain boundaries affect carrier transport adversely.^[30–32] These intrinsic defects can moreover introduce a hysteresis (in the current–voltage characteristics), which remains another area of concern in terms of the reproducibility of device characteristics.^[33–35]

Considering the significant influence of defects on light absorption, carrier extraction, and carrier transport in a hybrid halide perovskite-based device, it is hence essential to understand them as clearly as possible.^[36–38] Defect engineering in terms of controlling defect densities in the perovskites is therefore expected to emerge as an important avenue toward the improvement of device efficiency and reach the predicted limit.^[39–41] In this Review, we have aimed to collate established results on defect formation in the bulk of hybrid halide perovskites and at the interface with carrier transport layers and at grains and grain boundaries as well. Apart from summarizing some major advancement regarding different defect analysis techniques, we have collated a range of defect passivation approaches toward enhancing the PCEs of solar cells. This Review Article in effect points toward the prospects of defect engineering in perovskite materials to improve the PCE and long-term stability of hybrid halide PSCs.

2. Defects in Hybrid Halide Perovskites: An Overview

2.1. Origin of Defects and Defect Tolerance

The formation of defects is inevitable in solution-cast polycrystalline materials.^[42] Most of the halide perovskites are moreover formed through precursor routes in a solution-cast process, making the defects ubiquitous. As such, defects in a semiconductor can either exist in the form of shallow states close to the band edges and thus dope a semiconductor as a p-type or n-type or form deep-level midgap states which act as recombination centers.^[42] In polycrystalline MAPbI₃ films, electronic properties of the perovskite are greatly influenced by the presence of imperfections, such as intrinsic point defects, Schottky and Frenkel defects, grain boundaries, dislocations, and so forth.^[43]

Based on the formation type, intrinsic point defects in the bulk of MAPbI₃ are identified as 1) vacancy defects (V_{MA} , V_{Pb} , V_I), which are formed when an ion is absent from its allocated lattice site (MA: methylammonium), 2) interstitial defects (MA_i, Pb_i, I_i), where the ions reside at the interstitial positions of a lattice, and 3) defects arising due to the substitution of an atom with another atom, such as MA_{Pb} and Pb_{MA} alongside antisite substitutions, like MA_I, Pb_I, I_{Pb}, and I_{MA} (here MA_{Pb} represents a defect arising out of MA ion occupying a lead (Pb) site.^[25] These single-point defects can also appear as pairs, namely Frenkel and Schottky defects. While Frenkel defects are a combination of a vacancy and an interstitial defect of the same ions, Schottky defects, on the other hand, are formed with cation and anion vacancies.^[43] It should be keep in mind that a combination of defects can also create dynamic defect states such as edge location (1D) and grain boundary (GB) defects (2D).^[44,45] In **Figure 1**, we have illustrated all possible point defects in a 3D perovskite lattice (ABX₃), where yellow, purple, and blue dots represent the A, B, and X site, respectively, and green dots imply external impurity atoms.^[43]

A pioneering work in this direction has been conducted by Yin et al. to study the formation energy of all intrinsic defects in the bulk of the prototype MAPbI₃ perovskite.^[25] Their study revealed low formation energies for MA_i, V_{Pb}, MA_{Pb}, I_i, V_I, and V_{MA} defects with transition energies being less than 0.05 eV above the valence band maxima (VBM) or below the conduction band minima (CBM) and creating shallow-level traps. Among such possible defects, p-type V_{Pb}, n-type MA_i, and n-type V_I have been identified to be the most-dominant intrinsic defects in the bulk of MAPbI3 when formed in a CH3NH3I-rich and PbI₂-rich stoichiometry, respectively. It is worthy to mention here that it is the balance among all the possible defects that eventually dictates the Fermi energy in MAPbI₃, depending upon its compositional stoichiometry, and in turn explains the manifestation of bipolar conductivity (both p-type and n-type) observed in the perovskite.^[25,46,47] In MAPbI₃ perovskite, lead vacancies (V_{Pb}) are considered to be the most stable defects and are reported to exist in neutral and doubly negative charged forms.^[25,48] V_{Pb} defects in fact form in abundance due to energetically unfavorable antibonding interactions between Pb(s) and I(p) orbitals, leading to the breaking of Pb–I bonds.^[25] On the other hand, in case of MA_i defects, the methylammonium







cations (MA⁺) occupy interstitial positions on the facets of PbI₆ octahedra; a low formation energy of MA_i can be attributed to the weak van der Waals interaction of MA_i with Pb–I octahedra.^[25]

An interesting first-principle approach has been reported in the β -phase of MAPbI₃ toward the evaluation of Frenkel and Schottky defects in hybrid halide perovskites.^[49] The study estimated the formation energies of such defects and inferred that Schottky defects do not form trap levels inside the bandgap of the perovskite; however, they can still influence the device performance. It is worthy to state here that such an influence of Schottky defects on the performance of MAPbI₃-based solar cells has previously been reported through experimental studies.^[27]

2.2. Impact of Defects on Solar Cell Performance

The impact of point defects on the performance of solar cells is quite significant. Such defects can promote deep-level trap states for charge carriers and act as nonradiative recombination centers. Interestingly, such defects can form even in high-quality films, affecting the photovoltaic performance in an adverse manner.^[30-32] Fortunately, as mentioned earlier, the prototype MAPbI₃ has shallow defect levels and can be considered to be a defect-tolerant semiconductor.^[50] This unique property of MAPbI₃ is beneficial in designing solar cell devices as the possibility of trap-assisted recombination is low under this condition. However, such conclusions are based on first-principle density functional theory (DFT) calculations where periodic boundary conditions are important while studying defect physics. Based on different surface termination conditions, the shallow nature of the defects may disappear especially at the surface. Thus, defects formed at the surface, interface, and even at the grain boundaries can still limit the performance of devices. As the solution-processed perovskite thin films are polycrystalline by nature, the presence of defects at the grain boundaries in the perovskite absorber layer is inevitable and such defects eventually prompts trap-assisted recombination pathways in the otherwise defect-tolerant semiconductor.^[51] Numerous charged defects can also appear at the absorber layer due to dangling bonds and undercoordinated Pb2+ defects.[43] There are also possibilities of defect migration at the interface between a perovskite and carrier transport layers affecting the efficiency of carrier extraction in turn.^[52,53] Moreover, it is well reported that defect states in perovskites promote hysteresis in the current-voltage characteristics of the device.^[51] The stability of such devices based on perovskite materials can therefore have significant dependence on the type and density of defect states.^[28] According to a couple of recent studies, oxygen and moisture also promote defects in perovskites and thereby accelerate the degradation of respective devices.^[54,55]

Along with interfacial defects, deep-level defects are also associated with halide perovskite structures. The presence of deep-level trap states in ternary halide perovskites and also in double perovskites and defect-ordered perovskites remains a major point of concern towards the unsatisfactory performance of solar cells based on such absorber materials.^[8,32,56,57] As opposed to the self-healing property, which limits the density of defect states in MAPbI₃, the latter type of perovskites does not show the signature of extensive defect tolerance.^[56,58]

2.3. Different Defect Analysis Techniques

Defect physics in MAPbI₃ has so far been mostly explored by theoretical and simulation approaches based on DFT.^[25,49,59] A complex electronic structure of the material has however made such approaches quite nontrivial. It has been observed that different DFT approaches, such as semilocal–functional, hybrid–functional, or exchange–correlation functional on electronic structures, may yield different defect formation energies. The analysis of defects can similarly be influenced by the spin-orbit coupling (SOC) correction term in the material.^[60] The most accurate investigation regarding the nature and density of defects in MAPbI₃ can specifically be conducted through DFT approaches in a super-cell structure.^[61] In this super-cell approach, the calculations have been conventionally carried out by the following equation.

$$DFE(X)^{q} = E(X)^{q} - E(perf)\sum_{i}^{m} n_{i}\mu_{i} + q(E_{F} + V + \Delta V) + E_{q}$$
(1)

where $E(X)^q$ corresponds to energy of any super-cell having defect state *X* in a charge-state of *q* and *E*(perf) denotes the energy of a perfect super-cell. In Equation (1), n and µ represent the total number and chemical potential, respectively, of the element further added or taken away to the defect free system to form a defect. *q* represents the elementary charge of that defect. The term $q(E_F + V + \Delta V)$ symbolizes energy due to exchange of electrons with Fermi energy of the defective system for any shift in the electrostatic potential (ΔV) due to defects. The last term E_q denotes long-range coulomb interaction between periodic defects.^[61]

Molecular dynamics (MD) simulation is another computational method used to study the dynamic and structural properties of metal–halide perovskites.^[62–64] Theoretical studies as such can provide density of states (DOS), CBM, and VBM energies in a definitive manner and can therefore yield some useful information regarding the relative defect energies in perovskites with possible strategies toward defect engineering.

On the other hand, there are several experimental techniques to determine the defect densities and their influence on optoelectronic properties. We will discuss some of the commonly used techniques in this direction, such as photoluminescence (PL) spectroscopy, photothermal deflection spectroscopy (PDS), confocal fluorescence microscopy (CFM), thermal admittance spectroscopy (TAS), and scanning probe microscopy techniques like conducting atomic force microscopy (c-AFM), Kelvin probe force microscopy (KPFM), and scanning tunneling microscopy (STM).

2.4. Theoretical Studies of Defects

Theoretical studies of defect states in MAPbI₃ have predicted that energy levels of structural defects including iodine and methylammonium vacancies fall within two bands of MAPbI₃ without altering the bandgap.^[25] Another study has indicated that the charge imbalance created by methylammonium vacancy is often compensated by an iodine vacancy while retaining the charge



neutrality of the perovskite structure.^[49] As a result, electronic structures at the band edges are affected minimally with the electronic bandgap being preserved. Although the defect-tolerant nature of the material does not prevent defect formation, it ensures that defects with low formation energies are formed closer to the band edges instead of at the midgap. Such shallow defects hence contribute to overall carrier concentrations instead of deep-level nonradiative intraband trap states.^[45] Generally, radiative band edge defects are expected to form at very high concentrations; although beneficial for light-emitting diodes (LEDs), it is highly undesirable for solar cell applications. Defect-tolerant studies in other systems such as transition metal dichalcogenides and other semiconductors, as shown in Figure 2a,b, indicate that the tendency of a material to form defect states within the bandgap is primarily influenced by the similarity of orbital characters near the conduction and valence bands of semiconductors with antibonding valence band.^[65] In semiconductors with antibonding VBM, the defect states originating from vacancies/ interstitials are not generated inside the bandgap, leading to shallow defect states. Defect tolerance in MAPbI₃ is also attributed to the antibonding character of the VB. The VB of MAPbI₃ comprises contributions from Pb(6s) and I(5p) orbitals whereas the CB is mainly composed of Pb(6p) orbital.^[12] It can hence be speculated that 3D perovskites having an antibonding character of VBM are very likely to be defect tolerant in the bulk; however, experimental confirmation is yet to be achieved in this regard.

Structural and electronic properties of halide perovskites have been intensively examined using computational methods based on DFT. First-principle calculations based on DFT studies can provide information on the band structure, DOS of conduction and valence band charge densities, etc. In this direction, such computational studies on the defect properties of cubic MAPbI₃ crystals revealed that among such possible defects, p-type V_{Pb} and n-type V_I have been identified to be the mostdominant intrinsic defects in the bulk of MAPbI₃, having a



Figure 2. Band structures of the a) typical defect-intolerant semiconductor and b) the defect-tolerant (methylammonium lead iodide) perovskite. Reproduced with permission.^[201] Copyright 2017, American Chemical Society.

CH₃NH₃I-rich and PbI₂-rich stoichiometry, respectively (Figure 3).^[25] The transition energy levels of intrinsic acceptortype and donor-type defects in MAPbI3 are shown in Figure 3a,b whereas the formation energies of intrinsic point defects at chemical potentials are shown in Figure 3c-e. However, more in-depth calculations can be carried out considering different surface terminations during DFT analysis. The concept of the defect-tolerant nature disappears under this circumstance. In case of a thermodynamically stable CH₃NH₃Iterminated surface, the most stable defects are identified as a shallow-type V_{MA} irrespective of the growth condition. However, in case of I-rich stoichiometry, Ii-defects may also appear on this surface, which is considered to be located deep within the bandgap. On the other hand, for the same growth condition, a PbI₂-terminated surface would promote the formation of more Ii-defects leading to deep-level trap states.[44] Furthermore, DFT studies with different halide anions and monovalent cations confirmed that the defect landscape in these hybrid halide perovskites varies with composition; different perovskites have different dominant defects depending on their formation energy and balance among the possible existing defects.^[45]

In another notable study, DFT with generalized gradient approximation (DFT-GGA) calculations revealed the influence of Frenkel and Schottky defects on MAPbI3 and inferred that the Schottky defects do not form trap states in the bandgap.^[49] Similarly, an interesting study on the defect properties of MAPbI₃ through semilocal exchange correlation functionals, such as density functional theory-Perdew-Burke-Ernzerhof (DFT-PBE) calculations, concluded that most of the point defects in MAPbI₃ form shallow states (except I_i which forms deep-level states) and do not affect the electronic properties of the perovskite.^[66] However, charge trapping at I_i is limited by a kinetic barrier, resulting in long carrier diffusion lengths in MAPbI₃. They also estimated the defect properties in a mixedhalide perovskite, MAPbClI₂. In comparison with MAPbI₃, the mixed-halide perovskite has a reduced lattice constant and thereby an increased formation energy of iodine interstitials and hence the reduced possibility of formation of interstitial defects.^[66] Chlorine incorporation thereby improved recombination lifetime (a longer diffusion length) when compared with pristine MAPbI₃ and yielded a better cell performance in this mixed-halide perovskite and its analogues.^[61,67] The possible point defects in MAPbI3 are shown in Table 1 with their formation energies.

MD simulation is another computational method used to study the dynamic and structural properties of metal–halide perovskites. In MAPbI₃, such MD simulations have provided vital information regarding the role of iodine vacancies in trapping electrons in the perovskite (**Figure 4**a).^[68] Similar but independent studies using nonadiabatic MD simulations combined with the time-domain ab initio study have been reported to be effective in studying the role of iodine interstitial defects on hole trapping and recombination rates in MAPbI₃.^[69] A faster trapping and release of holes to the valence band through subbandgap iodine interstitial states has been evidenced in such studies (Figure 4b,c).

Computational methods based on DFT studies have been used to study the formation of defects and its consequences on the

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Figure 3. The transition energy levels of intrinsic a) acceptor-type and b) donor-type defects in MAPbI₃ and c-e) the formation energies of intrinsic point defects in MAPbI₃ at chemical potentials. In (c-e), defects with much higher formation energies are shown with dashed lines. Reproduced with permission.^[25] Copyright 2014, AIP Publishing.

Table 1. Possible point defects in MAPbI₃ along with their formation energies in electron volt for three different synthesis conditions.^[25] (The defect states with lowest possible energies have been marked in bold; those defects have the highest possibility of occurrence.).

Synthesis	Formation energy and effect on defect states											
condition	Acceptor like (p-type)						Donor like (n-type)					
	I _i	MA_{Pb}	V_{MA}	$V_{\rm Pb}$	I_{MA}	I _{Pb}	MA_{i}	РЬ _{МА}	VI	Pb_{i}	MA_I	Pbı
Iodine rich	0.23	0.28	0.81	0.29	1.96	1.53	1.39	2.93	1.87	4.24	3.31	5.54
Stoichiometric	0.83	1.15	1.28	1.62	3.01	3.45	0.93	2.51	1.27	2.91	2.25	3.62
lodine poor	1.43	1.47	2.01	2.68	4.34	5.10	0.20	1.74	0.67	1.85	0.93	1.97

electronic properties of metal-halide perovskites. Such studies also estimated the influence of external dopants and environmental interactions on the structural and optoelectronic properties of metal-halide perovskites. However, calculations based on DFT studies have some limitations and results may diverge depending on different approximations. Meggiolaro et al. used hybrid DFT, including dispersion corrections and SOC, to elucidate the changes in the optoelectronic properties of MAPbI₃ on exposure with iodine gas.^[61] However, methods like semilocal exchange correlation functional, such as the PBE exchange-correlation method, neglect the effect of SOC and self-interaction corrections and thereby provide a room to miscalculate the VB and CB energies and defect levels within the bandgap. The report concluded the use of hybrid methods (local density approximation [LDA] + U + SOC) for the more accurate estimation of defect states and the use of coulomb kernel functions (like HSE06) for shallow defects in MAPbI₃ perovskites.^[61]

2.5. Experimental Evidence of Defects

In the quest of experimental studies on defects in perovskite materials, various optical and scanning probe techniques have been used till date to deal with such defect states. The measurement of the trap-filled voltage in the space–charge-limited current (SCLC) method can be used to obtain the quantitative idea of the intrinsic defect density present in the perovskite.^[70,71] PL spectroscopy remains an interesting choice in this direction.





Figure 4. a) MD simulations and b) MD simulations combined with time-domain density functional theory to study the role of iodine vacancies in trapping electrons in MAPbI₃ and c) the schematic presentation of the mechanism for electron and hole trapping in MAPbI₃. a) Reproduced with permission.^[68] Copyright 2014, American Chemical Society. b) Reproduced with permission.^[69] Copyright 2017, American Chemical Society.

Steady-state and time-resolved PL (TRPL) spectroscopy have been reported as effective approaches to analyze the density of defects in metal-halide perovskites. Defects usually act as nonradiative recombination sites and quench PL emission: the lifetime of PL emission is also associated with trap density in MAPbI₃.^[72,73] Apart from PL, TAS is another novel approach to measure the trap-DOS (t-DOS), which can deliver sufficient information on both the deep and shallow defect states in perovskite thin films.^[74] PDS is also considered to be an important and sensitive technique to measure any weak absorption near the bandgap, where the information regarding the defect states can be obtained as well. As the fluorescence intensity is inversely proportional to the density of nonradiative defect states, CFM can also be successfully used to examine the defect states in a perovskite thin film.^[75,76] Scanning probe microscopy (SPM) is also another highly sensitive technique, providing an unprecedented opportunity to probe defect states through its much localized measurement approach.^[77–80]

2.5.1. Space-Charge-Limited Current

When trap states are present in a semiconductor, there is every possibility for injected carriers to become trapped at such states. Now, as the density of the injected carriers increases with an increase in applied voltage, more and more traps are filled with carriers; the voltage at which all traps are filled is called the trap-filled limit voltage. The measurement of the trap-filled limit voltage in the SCLC model is one of the common and straightforward methods to obtain a rough estimate of defect density in a perovskite material. In this approach, the defect density N can be estimated using the following equation.

$$N_{\rm defects} = \frac{2\varepsilon\varepsilon_0 V_{\rm TFL}}{eL^2} \tag{2}$$

where ε and ε_0 imply dielectric constant and vacuum permittivity of the perovskite, respectively, $V_{\rm TFL}$ denotes the trap-filled limit voltage, e is elementary charge, and L is thickness of the film.^[81] Following this technique, the approximate value of defect density in polycrystalline perovskite thin films turns out to be 10^{17} – 10^{19} m⁻³.^[70,71]

SCLC measurements can only be carried out in device architectures to detect the electron and hole traps by fabricating electron-only and hole-only devices. However, simultaneous measurements of both types of defects are not possible, yet the SCLC measurements are considered as one of the most widely used methods to characterize defects arising out of grain boundaries, surface or interface defects, and a few bulk point defects (Frenkel defects).^[82]

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2.5.2. Time-Resolved Photoluminescence Spectroscopy

PL measurements have a strong correlation with the nonradiative trap states and hence can be recognized as a potential tool to investigate the density of defects in hybrid halide perovskite materials.^[83-85] When illuminated during PL measurements, a perovskite material absorbs photons and produces e-h pairs. These photogenerated excess carriers can further emit light upon recombination. Now, by changing the excitation intensity, different PL responses can be plotted as a function of pump fluence in a double logarithmic scale. As the carrier dynamics is strongly influenced by intrinsic defects present in the perovskite material, an increment or a decrement of PL intensity at the steady state would imply reduction or enhancement of trap states, respectively. Under this circumstance, an abrupt change in the slope of the curve would be obtained, corresponding to the saturated trap density. The estimation of trap density can be obtained from the following equation^[86]

$$\eta_{\rm trap} = \frac{P_{\rm th}\alpha}{E} \tag{3}$$

where $P_{\rm th}$ is the threshold of pump fluence intensity at the saturated defect concentration, *E* the energy of photons, and α is the absorption coefficient. Moreover, the trap density can be obtained by fitting the TRPL data.^[83,84] The carrier lifetime from TRPL can be expressed as^[87]

$$\frac{1}{\tau_{\text{total}}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{nonrad}}} \tag{4}$$

where τ_{rad} and τ_{nonrad} denote radiative and nonradiative lifetime respectively. The total lifetime τ_{total} generally depends strongly on the second term, τ_{nonrad} , which is lower of the two lifetimes. Hence, a large effective lifetime infers a less trap-assisted nonradiative recombination and lesser defects. As compared with single crystals, polycrystalline perovskites possess a higher density of defect states, implying the existence of defects at the surface and grain boundaries.^[88]

Unlike the other defect analysis techniques, PL measurements do not involve any substrate per se. However, as PL emission is only collected by the detector, this technique is associated with surface defects.^[82]

2.5.3. Confocal Fluorescence Microscopy

As the intensity of fluorescence is inversely proportional to the density of nonradiative defect states in a perovskite thin film, CFM can be considered to be one of the significant methods to study the physics of defects in such materials. Here, the absence of fluorescence emission is considered to be a measure of defect states. It provides information on both the bulk and surface defects. It has some specific advantages over TRPL, which provides only an average value across the film.^[75] CFM provides a unique opportunity to probe the defects even in a particular domain in terms of the microscopic fluorescence mapping process. Here the defects can be viewed in the form of bright and dark domains. In a particular region, bright regions infer the

presence of lesser defects whereas dark regions suggest greater defect densities at a local scale.^[76]

In one of the pioneering work of its kind, Dequilettes et al. reported an enhanced PL intensity and lifetime in MAPbI₃ films placed in an inert environment.^[89] They used CFM and time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study MAPbI₃ films under a constant illumination and attributed the increase in PL intensity to be due to the reduced density of trap states in the bulk of the material. ToF-SIMS studies furthermore revealed iodine redistribution in MAPbI₃ films. They proposed that such photoinduced iodide migration passivated the iodide interstitials and iodide vacancies, leading to enhancement in the PL emission. They also combined CFM with scanning electron microscopy (SEM) to map the PL decay (**Figure 5**) and explored carrier decay dynamics in perovskite films.^[89]

It should be noted that this technique is only used to visualize the location of defect states. The types of defects cannot be identified from such measurements. The resolution of the asobtained CFM images is also considered as another limitation as the wavelength of excitation light is not comparable with the atomic scale.^[82]

2.5.4. Photothermal Deflection Spectroscopy (PDS)

In absorption spectroscopy, the wavelength dependence of the absorption coefficient at times consists of an exponential part called Urbach tail. Such a "tail" generally appears in poorly crystalline materials and in disordered/amorphous materials, as such materials have some localized states extending within the bandgap.^[90–92] By applying Urbach's empirical rule, the Urbach energy can be calculated from the following equation.

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_{\rm U}}\right) \tag{5}$$

where α is the absorption coefficient, α_0 is a constant, and E_U denotes the Urbach energy, which is correlated with the localized states in terms of width of the band tail. To obtain a straight line plot to calculate E_U from its slope, the equation can be rewritten as

$$\ln \alpha = \ln \alpha_0 + \frac{h\nu}{E_{\rm U}} \tag{6}$$

In this regard, PDS is a very sensitive technique to measure even a weak absorption near the band edges and provide vital information on the defect states; a lower value of E_U is an indication of having fewer defect states (**Figure 6**a). Basically, E_U is an important energetic disorder parameter, a change of which implies the existence of different energetic levels in the perovskite. Zheng and coworkers used hyphophosphorous acid (HPA) to passivate metallic lead defects. They have calculated the E_U using Urbach energy fit to the band edges (Figure 6b,c). A lower value of Urbach energy indicates a higher electronic order thereof.^[93]

It should be kept in mind that the Urbach tail is influenced by the temperature of the material and phonon interactions. Thus, it





Figure 5. Change in PL a) before and b–d) after exposure to simulated sunlight, e) three-color scale image showing dark, intermediate (Int.), and bright regions and f) local PL enhancement and relaxation for dark (blue, enhancement of 4.9×), intermediate (green, enhancement of 1.6×), and bright (red, enhancement of 1.1×) regions. The time (*t*) under illumination is highlighted in yellow and t > 0 shows the local PL relaxation dynamics over the time left in the dark. The dotted black line is the PL relaxation averaged across the whole fluorescence image. Reproduced with permission.^[89] Copyright 2016, Springer Nature.



Figure 6. a) PDS spectra of the perovskite film processed without and with HPA deposited on quartz substrates and calculation of the Urbach energy " E_{U} " for the perovskite film processed b) without and c) with HPA. Reproduced with permission.^[93] Copyright 2015, Springer Nature.

is important to conduct the control experiment at the same temperature. $\ensuremath{^{[82]}}$

2.5.5. Thermal Admittance Spectroscopy

Defect states are sometimes considered as capacitors as the trapping and detrapping nature of defect levels are analogous to the charging and discharging behavior of a capacitor. As a result, if an AC voltage is applied to a device, the admittance of the perovskite system depends on the frequency of the AC voltage. This simple concept is used in TAS that is basically used for the electrical characterization of capacitance and conductance in terms of frequency and temperature in a perovskite to study the defect levels.^[94,95] However, due to the temperature dependence, a deep-level trap may sometimes remain unavailable to contribute to the capacitance and conductance at a higher frequency, especially when the emission rate is comparably slower than the frequency.^[74,94] With an increasing temperature, the rate of emission from the trap increases, resulting in a higher contribution from the defects. In such a scenario, a threshold frequency appears in the form of steps and peaks in the temperature dependence of the conductance plot as a signature of deeplevel traps. The temperature of the inflection point for each capacitance versus the temperature plot at a fixed frequency is then drawn in the form of an Arrhenius plot of emission rate versus 1/kT. However, the energy distribution of defect states



can be obtained analytically using the following complex equation.

$$N_{\rm t}(E_{\omega}) = -\frac{V_{\rm D}}{qW_{\rm D}}\frac{\omega}{kT}\frac{{\rm d}C}{{\rm d}\omega} \tag{7}$$

where $V_{\rm D}$ and $W_{\rm D}$ are the potential barrier and depletion width, respectively, ω is the angular frequency, *C* the capacitance, *T* the temperature, and *k* is Boltzmann constant. This effective method can provide information on both shallow and deep defects in perovskite thin films.^[74,95]

This method has been found to be useful in probing surface or interfacial defects, defects due to grain boundaries, and point defects as well. However, the detection of deep traps near the Fermi energy is not possible due to the dependence of this technique with the trapping–detrapping mechanism.^[82]

2.5.6. Scanning Probe Techniques (c-AFM, KPFM, and STM)

Scanning probe techniques (microscopy) like c-AFM, KPFM, and STM have recently been used to study the electrical properties, band edges, and defect states in hybrid halide perovskites.^[9,32,46,79] c-AFM which is basically a modified version of AFM, having a conducting tip, can simultaneously measure the local I-V characteristics along with topographic images. Such I-V characteristics are generally obtained by applying a voltage in between the perovskite thin film and the tip of c-AFM. In this manner, the conductivity between the tip and the sample is also judged and could be mapped over a section of the film. Now, electronic conductivity can show contrasting behavior at the grain boundaries and interiors. Generally the grain boundaries present in perovskites are insulating in nature with a wider bandgap. Hence, their passivation promotes an increase in local conductivity. Such measurements thus provide unique opportunities to probe the effect of defect passivation by mapping the local conductivity of a semiconducting surface.^[96,97]

The surface work function of perovskite thin films plays a vital role in optoelectronic devices. The work function which has a key role in the transport mechanism across the Fermi energy can be derived from the surface potential. The distribution function of such a potential (potential has been fitted using Gaussian or Lorentzian function) generally represents the average surface work function,^[98] which can be obtained from the following equation.

$$eV_{\rm CPD} = \varphi_{\rm Tip} - \varphi_{\rm Sample} \tag{8}$$

where V_{CPD} is the contact potential difference (CPD) and φ_{Tip} and φ_{Sample} are the work functions of the tip and the sample, respectively. The work function of the tip is derived by scanning a reference or a standard sample like highly oriented pyrolytic graphite (HOPG) or gold. Similar to c-AFM, when the insulating GB defects are passivated, an increase in the CPD would be observed due to the enhancement of the conductivity and accumulation of charges at the surface as well. Hence, a combination of c-AFM and KPFM provides an unprecedented opportunity to confirm the claim of defect passivation in perovskite surfaces.^[78,99]

STM is another local mode of measurements where the differential tunneling conductance (dI/dV) spectra of the

semiconductors can provide the energy-dependent DOS of the perovskite.^[44,100] The DOS spectra obtained thereof can identify the energies of VBM and CBM of the semiconductor in the form of first peaks in both sides of Fermi energy $(E_{\rm F})$, which is considered to be aligned at 0 V. When a bias is applied to the tip, the first peak at a positive tip voltage will imply the withdrawal of electrons from the semiconductor and hence indicate the VB edge of the semiconductor; similarly, the first peak at the negative voltage will imply the injection of electrons to the CB edge of the material. As any kind of trap states situated within the bandgap can also contribute in such a tunneling process, their signature will appear nearer $E_{\rm F}$ as compared with their true band edges.^[32,44] The quantitative estimation of the defect states can be predicted from the magnitude of DOS obtained from the dI/dVspectra. The type of conductivity obtained from such analyses also provides important information on the nature of the defects (donor or acceptor). Similarly, the presence of many different defects can be viewed as a broader distribution of defect state energies in perovskite materials.

KPFM and c-AFM techniques can be useful tools to explore grain boundaries and surface defect states in hybrid perovskites. The setup for such measurements is shown in **Figure** 7a.^[101] The mapping of the CPD under various laser illumination intensities at a specified wavelength can be measured by KPFM (Figure 7b), whereas the current images of MAPbI₃ films under illumination can be recorded through c-AFM measurements (Figure 7c).^[102] Such studies have confirmed that ion migration in polycrystalline perovskite films occurs majorly through grain boundaries and also demonstrated the beneficial effects of the boundaries; the grain boundaries, instead of acting as recombination sites, act as carrier dissociation interfaces that in turn enhance the photocurrent in a device. KPFM has also been used to study the defect-induced band bending at the interface between a perovskite and an electrode.^[99]

However, it should be kept in mind that a proper electrical tuning of the tip for both c-AFM and KPFM is highly desirable, considering the sensitivity of such measurements. Moreover, in case of c-AFM, the general trend explained earlier is not always true. If a large amount of metal is diffused in the perovskite surface that is natural during the formation of undercoordinated lead defects, the conductivity would decrease after the passivation of such defects.^[78] Such a phenomenon would also show an opposite trend during KPFM measurements. Upon passivation, the CPD would decrease in a conflicting fashion due to a decrease in the surface conductivity.^[99]

STM and spectroscopic methods have been used to study the effect of doping on the electronic structure of the bandgap. Ohmann et al. conducted low-temperature STM studies on MAPbBr₃ single crystals and revealed the real-space atomic structure of the perovskite along with local defects and investigated the dislocation lines and surface defects.^[103] In another study, we have investigated the effect of self-doping in MAPbI₃ and FAPbI₃ perovskites (**Figure 8**) by varying precursor stoichiometry.^[46] This study demonstrated a gradual shift of the Fermi energy with a change in stoichiometry (from PbI₂-deficeint to PbI₂ rich-conditions), leading to a change in the electronic conductivity of the perovskite from p-type to n-type in nature. A variation in the stoichiometry of the precursor while forming a perovskite film leads to a change in the concentration







Figure 7. a) Illustration of the KPFM and c-AFM setup to explore grain boundaries and surface defect states in hybrid perovskites, respectively. b) Topography map, CPD images taken in the dark, and under various laser illumination intensities at a wavelength of 500 nm, intensity dependence of CPD in MAPbI₃ at a wavelength of 500 nm as measured by KPFM. (c-AFM measurements were carried out on a glass/FTO/TiO₂ structure over an area of 5 μ m²) c) Topographic image, current image taken in the dark and under illumination at 0 V and under illumination at 0.3 V. Insets in panels of (c) show overlaps of the corresponding c-AFM maps and a topography map of the region with a white outline (wavelength and intensity of the illumination were 500 nm and 1.1 kW cm⁻², respectively.) Reproduced with permission.^[101] Copyright 2015, American Chemical Society.



Figure 8. a) dI/dV spectra and b) band diagram of MAPbI₃ films with different PbI₂ and CH₃NH₃I (MAI) stoichiometries as mentioned in the legends. Reproduced with permission.^[46] Copyright 2018, American Chemical Society.

of electrons and holes in the perovskite; in other words, the stoichiometry controls the presence of point defects in the perovskite in which a low PbI_2/CH_3NH_3I ratio would amount to a PbI_2 -deficient environment, leading to the formation of a large



Table 2. Experimer	tal techniques	used to	probe	specific	defects
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Technique	Mode of measurement	Sample	Defects probed	Limitations	Ref.
SCLC	Electrical	Electron- or hole-only devices	GB defects, surface defects, interfacial defects, point defects.	Device architecture is needed. Simultaneous measurement of hole and electron traps is not possible.	[81,82]
TRPL	Optical	Solid/liquid/film	Surface defects	Point defects are difficult to probe.	[83,86]
CFM	Optical	Film	_	Only the position of the defects can be probed.	[82,89]
PDS	Optical	Film	Localized point defects	Temperature sensitive	[93]
TAS	Optical	Film	Deep defects, antisite defects, GB defects, surface defects, interfacial defects	Existence of shallow defects is not possible to probe.	[95]
SPM	Electrical	Film	GB defects, surface defects, interfacial defects, point defects	Sensitive in ambient condition. Proper electrical tuning of cantilever and tip is necessary. Energetically mapping of defects is not possible.	[97,103]

number of lead and iodine vacancies. Now, as the formation energy of lead vacancies is much lower than those of the other existing point defects, the former one would dominate and a balance among these existing point defects will mark the Fermi energy for the particular composition of the perovskite (p-type conductivity). Similarly, under a CH_3NH_3I -deficient environment, that is a PbI₂-rich environment, three kinds of point defects were formed in films: lead interstitials, methylammonium vacancies, and iodine vacancies. Among them, iodine vacancy has the least formation energy and a balance among the three defects inferred an n-type behavior in the respective thin film. Thus, studies on the shift in Fermi energy could infer not only the presence of point defects but also the nature and type of defects in hybrid halide perovskites.

We have summarized different experimental defect analysis techniques, as shown in **Table 2**.

3. Defect Passivation in ABX₃

As mentioned earlier, the defects states have a detrimental effect on device performance. Hence, the passivation of defects is necessary to boost the PCE of solar cells. In this section, we will discuss different strategies to passivate defect states in perovskites, having a beneficial effect in PSCs. This includes passivation techniques in the perovskite absorber layer through compositional engineering and doping, different surface passivation treatments such as Lewis acid and base treatments, interfacial passivation, and different physical passivation processes.

3.1. Materials Engineering

As stated earlier, one of the wonderful properties of the $MAPbI_3$ structure is its defect-tolerant nature. Most of the intrinsic defects in $MAPbI_3$ form shallow states close to band edges and do not contribute to the optoelectronic properties of devices based on the material.^[50] However deep-level defects, grain boundaries, ion migration, and interface defects are reported to adversely affect the stability of the material as well as optoelectronic properties of the devices based on the perovskite. Different passivation techniques have been developed with an aim to reduce the detrimental effects of defects in the material and improve the stability and performance of MAPbI₃-based devices. Various chemical and physical passivation methods have been considered in this respect. Composition engineering in forming mixed-cation (MA, FA, and cesium) and mixed-anion (chloride, bromide, and iodide) perovskites has been reported to be an efficient method to improve performance and stability of perovskitebased devices. The characteristics of high-efficiency solar cells containing such mixed perovskites as the absorber layer have shown that they possess lower defect densities and also have a high defect tolerance. In this regard, the addition of cesium in FA_{0.83}MA_{0.17}Pb(I_{0.83}Br_{0.17})₃ has been reported to reduce the defect densities by one order of magnitude.^[104] The addition of bromides to form mixed-halide perovskites has been reported to transform the deep-level iodide interstitial defect states to shallow defects by shifting their energies closer to the VB. Such treatment can remove metallic lead from the lattice, resulting in an enhancement of carrier lifetime.^[105]

Metallic lead defects (Pb⁰) can originate in MAPbI₃ films due to a number of possible reasons, such as excitation stresses,^[106] incomplete reaction or loss of halides during the reaction process,^[107] contamination to the precursor or solvent, aging stresses.^[45] and so on. These lead-defects introduce nonradiative pathways, which act as quenching centers of excitons (reduction of PL quantum efficiency), hamper device performance, and also stop the long-term stability of perovskite devices.^[108,109] The formation of such Pb⁰ defects in MAPbX₃ can be prevented by increasing the concentration of CH₃NH₃X in the precursor, that is, through a deliberate PbI2-deficient condition of the reaction, introducing redox-active organic molecules, oxidizing agents, and so forth.^[45] Zhang et al. reported the passivation of uncoordinated lead ions and iodine vacancies in an all-inorganic perovskite through additional anionic dopants like chloride, which is known to reduce the defect density and also improve the morphology of perovskite crystals.^[110] It has been reported that even when stoichiometric precursors are used to form MAPbI₃, metallic lead remained in the films due to the incomplete reaction or loss of halides during the reaction process. These lead residues introduce nonradiative pathways and quench the PL intensity of the perovskite.^[108] The formation of metallic lead in MAPbX₃ can be prevented by increasing the concentration of methylammonium halide in the precursor, that is, through a deliberate PbI_2 -deficient condition of the reaction. Zhang et al. reported the passivation of uncoordinated lead ions and iodine vacancies in an all-inorganic perovskite through additional anionic dopants like chloride, which is known to reduce the defect density and also improve the morphology of the perovskite crystal.^[110]

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Nonstoichiometric compositions leading to PbI2-rich and PbI₂-poor growth conditions have also been reported to modify the defect states in MAPbI3 perovskite. The effect of excess PbI2 in the perovskite is controversial; some researchers have inferred that excess iodine has a detrimental effect on perovskite films whereas others have claimed PbI2 to act as a defect-passivating agent. A straightforward method in this regard is self-doping, which can be useful for efficient defect passivation in MAPbI₃. An addition of excess PbI₂ was found to be effective to passivate local grains.^[111-113] PbI₂-rich conditions have also been reported to reduce defect densities at the perovskite interfaces and improve the crystallinity of perovskite films, leading to improved efficiencies in MAPbI₃-based solar cells. The growth condition with PbI₂-poor precursor stoichiometries, in contrast, reduces the deep-level iodine interstitials in MAPbI₃, leading to improved PL emission.^[29] Chen et al. have recently reported an in situ passivation strategy, utilizing excess PbI₂ to passivate the defects at the perovskite surface and grain boundaries.^[113] As far as the role of iodine is concerned, the introduction of excess iodine in the precursor solution through the use of CH₃NH₃Irich precursors has been reported to reduce deep-level defects. The addition of iodine led to the formation of I_3^- , which passivated iodine vacancies.^[45,85] However, the amount of excess iodine has to be optimized to achieve an optimum performance. We would like to mention here that defect passivation through excess iodine can be accomplished by adding both excess CH₃NH₃PbI₃ and PbI₂ in the precursor. However, the use of excess CH₃NH₃PbI₃ has been reported to be more beneficial in this regard as the neutralization of negatively charged iodine defects through positively charged MA⁺ forms volatile CH_3NH_3I , whereas the use of Pb^{2+} results in the formation of wide-bandgap PbI₂ with insulating grain boundaries.^[85] Such a passivation process effectively improves the stability of PSCs along with boosting the PCE to over 22%.^[85] In a recent work, Wang et al. reported that antisolvent-washing treatment with excess iodine can be beneficial to enhance the PCE of solar cells, as such a treatment promotes better crystallization and defect passivation of undercoordinated \mbox{Pb}^{2+} defects and dangling bonds.^[114] Inference from work using excess PbI₂ has remained inconclusive as there are reports of light-induced defect formation in the perovskite synthesized with PbI2-rich precursors.[115]

3.2. Extrinsic Doping

3.2.1. Inorganic Dopants

Metal-halide perovskites are mostly synthesized through facile solution-based approaches. The addition of inorganic dopants to the reaction mixture is one of the most widely explored methods for external doping and defect passivation. In general, the vast majority of charged defects, such as cation vacancies, halide vacancies, and antisite defects, is passivated using an additive with the opposite charge. However, this is not true for all the cases as defect passivation can also be conducted, following replacement by similarly charged ions. Although a number of trivalent elements such as bismuth, indium, antimony, gold, etc. have been introduced as dopants in MAPbX₃ (X = I and Br) structures, efforts have mostly resulted in the tuning of electronic structures of the parent perovskite. Among the possible trivalent dopants, bismuth doping has been studied extensively due to multiple aspects of such heterovalent doping. Bismuth has been reported to be an extremely effective means for bandgap tuning (redshift to be specific).^[116] In addition, at low concentration of doping, Bi³⁺ dopants have been found to fill the trap states and improve ionic conductivity of the perovskite; at a higher concentration of doping, they act as nonradiative recombination centers, leading to a transition from bimolecular recombination in pristine MAPbX₃ perovskites to a dominant trap-assisted monomolecular recombination process.[117,118]

Abdi-Jalebi et al. reported doping of MAPbI₃ with monovalent cations (Na⁺, Cu⁺, and Ag⁺) having an ionic radius similar to that of bivalent lead cations. Such heterovalent substitution has led to an improvement in the PCE of solar cells based on doped materials.^[119] The improved performance upon doping of a monovalent cation has been attributed to a notable decrease in charge transport activation energy through the passivation of MA⁺ vacancies by the filling mechanism and thereby an enhanced electron and hole mobility.^[119]

Among all the inorganic dopants, K⁺ has been found to be the most suitable candidate, as it can easily accommodate itself in the interstitial position instead of substituting the lead ions. Moreover, it has several useful impacts after the passivation of halide vacancies through immobilizing or the vacancy-filling process, as it can arrest iodine migration and reduce hysteresis in the current-voltage characteristics of solar cell devices.^[120] Experimentally, passivation of both positive and negative charges in alloyed perovskites has also been achieved through substitution by potassium and rubidium ions. These ions have a smaller effective ionic radius to occupy interstitial sites and surfaces. Such a substitution enhanced the PL emission and charge transport in these doped halide perovskites. In similar studies, Nam et al. reported the incorporation of K⁺, leading to an improvement in PCE, stability, and the reduction of hysteresis in the current-voltage (I-V) characteristics of solar cells.^[121] Tang et al. studied the effect of various alkali-metal cations on the structural and electronic properties of $FA_{0.85}MA_{0.15}PbBr_{0.45}I_{2.55}.^{\left[122\right]}$ They reported least defects upon K⁺ doping in the perovskite, with an upward shift in both CBM and VBM energies. Such an improvement can be ascribed to the inhibition of iodine ion migration and reduction of bulk and interfacial trap densities by potassium ions, leading to a narrowing of hysteresis in the current-voltage characteristics. With potassium iodide (KI) inclusion in the precursors, Abdi-Jalebi et al. have reported an interesting approach of defect passivation where K⁺ ions could passivate the halide defects in the perovskite absorber layer. A schematic illustration of halide vacancy passivation is shown in Figure 9a. In this way, upon an increasing concentration of KI in the precursor, they have reported an improvement in the PCE from 17.3% to 21.5% in devices based on (Cs,FA,MA) Pb(Br_{0.15}I_{0.85})₃ perovskites with a significant increase in the

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Figure 9. a) Schematic representation of the defect passivation process through KI doping and b) J-V characteristics and variation of short-circuit current density (J_{SC}) and open-circuit voltage (V_{OC}) with a fraction of potassium in (Cs,FA,MA)Pb(Br_{0.15}I_{0.85})₃-based solar cells. Reproduced with permission.^[202] Copyright 2018, Springer Nature.

open-circuit voltage (V_{OC}) (Figure 9b). Recently, the incorporation of Cs⁺ and K⁺ has been reported to be effective for obtaining phase-pure and defect-free perovskite absorber layers.^[123] The incorporation of KI in the precursor is also reported to reduce iodide Frenkel defects in MAPbI₃. The dopant metal ions could passivate anionic defects in the perovskite through electrostatic interaction and formation of ionic bonds with negatively charged defects.^[120] The reduction in the density of defects in MAPbI₃ has also been achieved through aluminum-ion doping. Such methods effectively reduced the microstrain in the doped MAPbI₃ crystals, resulting in a reduced hysteresis and an improved PCE in devices based on the doped material.^[124]

3.2.2. Organic Dopants

Passivation of defects can similarly be attempted with a set of organic dopants or additives. Fullerenes (PCBM) can be mixed with the precursors to passivate donor-like Pb-I antisite defects through the formation of coordination bonds in the PCBMhalide complexes.^[45] Moreover, PCBM can heal iodine-rich trap states and prevent iodide ion migration under the influence of an electric field. The process increased the PCE of respective solar cells by 1.5 times.^[125] Guanidinium (GA)-based additives in MAPbI₃ also have passivation capability of ion vacancies, enhancing the carrier lifetime and achieving a high V_{OC} thereby. It also helps to reduce recombination at the interfaces and provides a protective shield to resist oxygen intrusion. De Marco et al. observed a significant improvement in the PCE from 16.3% to 17.1% by incorporating GA in the precursor solution.^[83] The addition of the electron-donating polymer, namely PCDTBT, was found to be beneficial to reduce the defects in the perovskite system. Zhang et al. have observed that as compared to a PCE of 13.2% in pristine devices based on mixed-halogen perovskites,

the modified devices with PCDTBT showed an improved efficiency of 16.8%. The lone pair of the polymer combines with the undercoordinated defects and passivates them.^[126] Many of such organic additives are better categorized as Lewis acid-base passivators and have been explained in a following section. Wang et al. have doped imidazolium (IA) at the A-site of ABX₃ structure and casted thin films of defect-free perovskite with a compact film morphology. They have observed an increase in carrier lifetime and suppressed ion migration due to the passivation of negatively charged vacancies. In this approach, they became successful to achieve a PCE of 16.0% in an inverted geometry.^[127] The incorporation of methylammonium (MA)-based additives seems to be effective as well. Apart from an improvement in the PCE of solar cells, MA exerted an additional effect on negatively charged vacancies and antisite defects; the ions via the disproportionation reaction could also counter residual oxidized I₂, which stimulated trap states. Interestingly, in such approach, the Pb/I ratio was not disturbed.^[81]

3.3. Surface Passivation

3.3.1. Lewis Acid-Base Reaction

Undercoordinated lead and halide ions at the perovskite surface along with dangling surface bonds reduce the stability of the materials and also the efficiency of perovskite-based devices. Lewis acids and bases, which can accept and donate a lone pair of electrons, respectively, are commonly used as a passivating material to reduce the effects of ionic defects in perovskites (**Figure 10**).^[97,128]

Derivatives of amines, carboxyl, hydroxyl, carbonyl, and phosphine oxides with a lone pair of electrons are being used to passivate defects in metal–halide perovskites.^[128–130] The lone pair of electrons on Lewis bases passivates the undercoordinated





Figure 10. a) Schematic illustration of the interaction of π -conjugated Lewis base and lead (Pb), b) formation of a dative covalent bond between two atoms, and c) schematic of passivation of trap states. Reproduced with permission.^[81] Copyright 2016, John Wiley and Sons.

lead ions by forming coordination with them and thereby improving the optical and electronic properties of such passivated perovskites. Such a Lewis acid-base adduct approach was followed by Park and his group by dissolving the precursors in polar aprotic solvents.^[131] As polar aprotic solvents bear oxygen, sulfur, or nitrogen, they can act as a Lewis base; the other component of the precursor, namely PbI₂, which is known to be a Lewis acid, has a chance to form an adduct by reacting with the Lewis base.^[132] These Lewis base-Lewis acid adducts between perovskites and solvent groups led to the formation of highly crystalline large grains with improved carrier lifetime. Therefore, it can be noted that the typical route of perovskite precursor preparation is based on dissolving PbI₂ (Lewis acid) with DMF/DMSO (Lewis base solvent) and supersaturating it to force rapid crystallization.^[133] In another study, Lee et al. have reported a high efficiency in MAPbI₃-based solar cells with urea, a bifunctional Lewis base, which passivated the grain boundaries and initiated grain growth.^[134] Lin et al., on the other hand, have introduced a layer of π -conjugated Lewis base indene derivative (IDIC) on MAPbI3 counter-electrode interfaces. The functional groups (C=O and C \equiv N) of IDIC strongly interact with the undercoordinated Pb²⁺ at the surface and passivate the trap states, reducing the defect densities and improving the charge extraction and carrier transport.^[81] Similarly Noel et al. showed that sulfur donors of thiophene and nitrogen donors of pyridine could be used for passivating such defects at the surface, followed by an improvement in the solar cell performance.^[128-130] Graphene is another carbon allotrope used as a defect-passivating material in perovskites. Hadadian et al. reported defect passivation by adding nitrogen-doped graphene in the precursor solution of perovskites. Here, graphene is reported to reduce nonradiative recombination pathways by passivating positively charged surface defects through the Lewis base property of nitrogen.^[135] Other 2D materials in this direction include graphene oxide and reduced graphene oxides. Li et al. reported passivation of perovskites with chemically modified graphene oxide and reported an enhancement in the PCE and stability of PSCs. They attributed the passivating effect to be due to an interaction between 4-fluorophenyl function groups of the 2D material with uncoordinated lead ions of the perovskite.^[136] In this direction, thiophene, pyridine, and EDT have been proven as the most appropriate Lewis bases.^[128–130] Among them, pyridine has the most powerful impact as it can form the strongest bond at the perovskite surface and passivate undercoordinated Pb²⁺ defects.

Similarly, Lewis acids are used to passivate negatively charged undercoordinated halide defects. Carbon allotropes like fullerenes have exhibited excellent electron-transport properties and are reported to improve stability, reduce hysteresis, and improve the PCE of perovskite-based devices.^[51] Highly electronegative fullerenes exhibit excellent electron-accepting properties. Functionalized fullerenes are reported to bind to uncoordinated atoms of the perovskite surface, passivating the surface defects in the perovskite. Shao et al. reported the use of PCBM as a Lewis acid-passivating material in MAPbI₃-based devices.^[51] They attributed the improvement in device stability as well as solar cell parameters to be due to the passivation of electron-rich defects through PCBM by forming ionic bonding. Here, fullerenes are also reported to passivate Pb–I antisites in perovskites and reduce surface charge recombination pathways, resulting in a narrowed



hysteresis in *I*–*V* characteristics. Similarly, Tian et al. evaluated the effect of functional groups on fullerene derivatives and reported that the addend structure and functionality can influence the passivation ability of perovskites.^[137] However, although a wide range of fullerene derivatives have been considered for passivating defects in perovskites, the perovskite–fullerene interaction is not yet completely understood. In this direction, IPFB has been reported to be an efficient Lewis acid, which can passivate the undercoordinated I⁻ with the formation of supramolecular halogen bonds.^[129]

Zang et al. reported the synergistic effect of a Lewis acid and Lewis base dual system; they investigated the effect of bis-PCBMmixed isomers as a Lewis acid and bromophenyl–thiourea as a Lewis base. They have reported the passivation of deep-level traps as the Lewis acid accepts electrons from Pb–I antisites, whereas the Lewis base passivates the Pb²⁺ ions.^[138]

3.3.2. Interfacial Passivation

As stated earlier, $MAPbI_3$ can be considered as a defect-tolerant compound. However, a large number of charged defects may form at the absorber layer surface and also in between material interfaces. As a result, researchers took interest in developing effective passivation methods to reduce such defects. Apart from different postdeposition techniques, two effective methods are considered in this direction.

Introduction of Passivation Layers: Introduction of a passivation layer in between the perovskite absorber and the charge transport layer is a common technique to reduce the defect density. This method is somewhat complex but is favourable to achieve high-efficient solar cell devices. Such a passivation layer can be introduced at the interfaces with both the ETL and HTL of solar cell architectures. Depending on the locations of the passivation layer in a device configuration, they are classified and discussed.

To reduce interfacial charge recombination due to surface defects, a few passivation layers are introduced in between the perovskite layer and HTL. In this direction, the most common passivation technique is the addition of MABr and FABr which can act as an intermediate phase to the perovskite $APbI_{3-x}Br_x$ (A = MA or FA) on top of the perovskite layer.^[72,139] The excess MA⁺ and FA⁺ can also passivate defects and compensate the loss due to charged defects arising out of an annealing process. It may be noted that, due to such a treatment, no new perovskites are formed; only a thin layer of the intermediate perovskite phase with a composition gradient is created. Recently, Yao et al. reported the introduction of ethylene amine derivatives with different ligands, which form a capping layer on top of the perovskite, acting as an interfacial passivation layer to boost the efficiency of solar cells.^[140] Similarly, phenethylammonium iodide containing different functional groups seem to be useful as it creates an ultrathin layer of a 2D perovskite phase, where the electrostatic interaction between the benzene ring of phenethylammonium group and undercoordinated Pb²⁺ ions increases the efficacy of passivation.^[141] The introduction of a polymer interlayer, namely polydimethylsiloxane (PDMS) in between the perovskite and HTL, has been found obliging, due to the cross-linking behaviour of the polymer in reducing the interfacial charge recombination.^[142]

Similarly, the passivation layer can be situated in between the perovskite film and the ETL. Fullerene has been considered to be a very useful passivation agent in this context. A double layer of fullerene can serve as both ETL and an interfacial passivation layer and has been found to be beneficial to reduce the hysteresis in the *I–V* characteristics of solar cells.^[51] Zheng and coworkers recently observed that the undercoordinated Pb^{2+} can be passivated by the amide group of fullerene derivatives, resulting in a high $V_{\rm OC}$ in solar cells.^[143] In this regard, the most powerful agent is certainly quaternary ammonium halides having the zwitterion structure that can passivate both positively and negatively charged defects in the perovskite simultaneously. Zwitterion molecules such as choline chloride can effectively heal both types of defects by their separated positive and negative part to enhance V_{OC} without losing short-circuit current-density (I_{SC}) and fill factor (FF).^[71] Li and coworkers have reported CsBr to be a suitable candidate for interfacial passivating agents between ETL and the perovskite absorber as the passivating material can reduce the work function of TiO₂ and simultaneously promote uniform crystallization of the perovskite layer to finally suppress the GB defects.^[144] In this context, poly(methyl methacrylate) (PMMA) has also been used efficiently as a passivation layer which can concurrently reduce the defects originating from dangling bonds at the perovskite-TiO₂ interface and shield the TiO₂ layer from oxygen adsorption.[145]

Recently, Chen et al. demonstrated the effect of bifacial defect passivation by introducing thioctic acid which can chemically anchor to the perovskite surface in forming a polymer due to its crosslinking behaviour.^[146] The polymer layer can passivate the interfacial defects present in between the perovskite and both the charge transport layers. Similarly, Mahmud and coworkers reported a double-sided passivation strategy by incorporating bulky organic cations which form the thin surface layer in both sides of the perovskite in a sandwiched device structure to promote the dual passivation method.^[147]

Usage of New Transport Layers: The defects exist not only in the interfaces between the perovskite and a transport layer but also in the transport materials themselves. In the past few years, many modified charge transport layers are introduced in perovskite solar cells with a reduced defect density. TiO₂ can be considered to be a suitable candidate among all the traditional ETLs in highly efficient solar cell architectures. However, the presence of Ti³⁺ can serve as defect states and can hinder charge separation at the TiO2-perovskite interface.^[53] In this direction, amine-mediated TiO₂ (AM-TiO₂),^[148,149] chlorine-capped TiO₂ (TiO₂-Cl),^[150] and defective-TiO₂^[144] have been introduced. They were found to be beneficial to heal the defects in the parent TiO₂ compound. Moreover, the application of such modified compounds in solar cell devices has been found to be better than that of TiO₂. Similarly, SnO₂, which is commonly used as an ETL, is benign in defect states due to Sn⁴⁺. Recently, Jung et al. have used SnO₂-KCl composite as an ETL and observed an increase in the PCE of perovskite solar cells. Such an improvement has been explained in terms of defect passivation in the SnO₂ layer.^[151] Passivating defects in a HTL has also been considered to be a major approach to promote the PCE of perovskite solar cells. As such, the most commonly used HTL, spiro-OMeTAD, is responsible for the degradation of perovskite solar cells due to its inherent defects. Passivation of defects in spiro-OMeTAD

through doping is however costly.^[152] Moreover, this compound has little role in passivating defects of the perovskite layer. Numerous HTLs have therefore been introduced to encounter these issues; copper phthalocyanine (CuPc) and conjugated polymers such as PCDTBT can be useful to passivate the defects in a HTL.^[153,154]

3.3.3. Physical Passivation Methods

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Apart from chemical modifications of a perovskite structure, physical treatments of perovskite films can also reduce defect density and improve the performance of perovskite-based devices. In this section, we have discussed a few physical passivation methods to passivate the defects in perovskites. These techniques are simpler and more straightforward as compared with chemical modification processes. Moreover, the methods are almost independent of the choice of perovskite material and device configuration.

Light: One such example is light-induced passivation of defects in perovskites. Photons have dual effects on the defect states; they can heal defects and at the same time can create new defect states.^[155] Dequilette et al. reported photoinduced enhancement in PL emission in perovskite thin films.^[89] They attributed this enhancement to be due to an order of magnitude reduction in the trap density of perovskite layers. They proposed that under illumination, photoexcited electrons passivated the surface vacancies, leading to a change in the internal electric field prompting iodide migration. The iodide migration fills up vacancies and reduces the density of defect states and thereby nonradiative recombination pathways, improving PL emission from the perovskite crystals. In another report, Mosconi et al. reported light-induced annihilation of $(V_I)^+/(I_i)^-$ Frenkel defect pairs in MAPbI₃ thin films.^[156] However, there is a limitation of this approach as defect healing can only be facilitated through the low migration energy of iodine-related defects only.

Heat: Defect states generally appear due to the loss of periodicity in the crystal lattice during synthesis through solution process. Application of heat can recover the periodicity as such perturbation can rearrange lattice and also improve the film quality. In addition, the organic cation (MA⁺ or FA⁺) is evaporated during the annealing of the film, making the perovskite into a PbI₂-rich one, which can further passivate the defects at the surface; advantages of such self-passivation methods have been discussed previously. However, optimization of the annealing temperature is very much important as pinholes are generated at higher temperatures, which can increase the defect density further. In this regard, a thermal treatment for 10–30 min at 150 °C has been found to be suitable for MA- and/or FA-based perovskite materials.

Hot Casting: Similar to the thermal treatment technique, hot casting method also possesses unprecedented opportunities in passivating surface and GB defects. Unlike thermal annealing, in a hot casting method, heat is applied during the spin casting method. Hot casting of perovskite films improves crystallite size and reduces trap states at the surface and bulk defects as well. It may be recalled that defects can be associated with pinholes, surface roughness, and grain size of the perovskite layer.^[157] It has been found that such technique is capable of growing

mm-sized grains which are highly desirable for the large-scale production of perovskite solar cells.

Vacuum and Solvent-Assisted Annealing: Li et al. reported the vacuum-assisted annealing of perovskite films for the effective removal of volatile degradation byproducts and to improve crystallization in perovskites, leading to a higher PCE in solar cells.^[158] In another study, Xiao et al. reported the solvent-assisted annealing of perovskites under dimethyl formamide (DMF) vapor. The schematic diagram of such a solvent-assisted annealing process is shown in **Figure 11**a. They reported an improvement in the crystallization of MAPbI₃ and PCE of devices; solvent-annealed films yielded crystallites as large as 1 µm, which were observed from SEM images, as compared with 260 nm crystallites obtained upon a usual thermal-annealing process (Figure 11b).^[74]

Antisolvent-Assisted Crystallization: The application of the antisolvent during spin coating process is another mostly used technique to increase crystallization which further reduces the defect density. However, proper selection of the antisolvent toward perovskite film fabrication is crucial in this regard as some of the chemical groups present in antisolvent may affect perovskite formation. In general, antisolvents with low boiling point, high vapor pressure, and good polarity are suitable in this method.^[159] Similarly, antisolvent vapor such as alcohol and dichloromethane (DCM) can also used widely to prepare large-grain perovskite thin films.^[160]

3.3.4. 3D Perovskites Passivated by 2D Perovskites

2D perovskites have recently witnessed an enormous progress in terms of stability due to an effective protection by hydrophobic organic spacer cations.^[161] However, due to their large optical bandgap and anisotropic and inefficient charge transport caused by such long organic spacer cations, the PCE of solar cells based on pure 2D perovskites is still inferior as compared with their parent 3D analogues.^[162] Hence, the application of the pure 2D Ruddlesden-Popper or Dion-Jacobson phase in solar cell structures and defect physics in such systems has not gained momentum as compared with double or triple perovskites. However, the hybridization of 2D and 3D perovskites is turning to be a promising pathway.^[161,163] Recently, a desired stability of 2D perovskite has been combined with the superior lightharvesting properties of 3D perovskites to fabricate highly efficient solar cells having long environmental stability simultaneously. In this section, the significant role of 2D perovskites, either as an additive or as a passivation layer, has been discussed. In this context, the Ruddlesden–Popper $(RNH_3)_2(A)_{n-1}BX_{3n+1}$ phase of the perovskite has been the focus.^[162] 2D perovskites have recently been found to offer dual roles, as it can protect a MAPbI₃ layer from thermal degradation and can prevent ion migration as well.^[164] In this direction, the reaction of a longchain organic spacer, namely butylammonium (BA) with MAPbI₃, has been found to passivate defects; the defective surface of the 3D perovskite can be healed by the 2D counterpart yielding a PCE of 22.5% in MAPbI₃-based devices.^[164] Similarly, Wang et al. have recently introduced BA in a 3D perovskite to form $(BA)_x(FA_{0.83}Cs_{0.17})_{1-x}Pb(I_{0.6}Br_{0.4})_3$; it has been observed that the 2D phase was helpful to enhance the

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Figure 11. a) Schematic representation of solvent-assisted thermal annealing and b,c) its effects on perovskite films. Reproduced with permission.^[74] Copyright 2014, John Wiley and Sons.

crystallinity by reducing crystal defects and suppressing nonradiative recombination pathways.^[165] The use of alkylammonium halide has led to the formation of 2D–3D hybrid perovskites with the 2D perovskite passivating the defects of 3D ones.^[166] The 2D–3D-heterostructured perovskites thus showed an enormous promise in the fabrication of gradient perovskite films. Yao et al. recently reported the incorporation of similar bulky cation-containing ethylene amine ligands which can create an ultrathin layer of 2D perovskite at both sides of a 3D perovskite to heal the defects at grain boundaries.^[140]

In **Table 3**, we have summarized different types of commonly used defect passivation approaches in APbX₃.

4. Defects in Perovskites Beyond ABX₃ and Their Passivation

4.1. Perovskites Beyond ABX₃

To address the toxicity of lead in perovskite materials for solar cells, focus has always been toward lead substitution in MAPbI₃ with suitable elements having isoelectronic configurations (s^2p^0), which is often believed to be one of the major factors in achieving superior optoelectronic properties in the

material.^[8,167,168] Through combinatorial approaches, trivalent metal-based ternary perovskites (A3B2X9) and double perovskites in the form $A_2B'B''X_6$, where B' and B" are monovalent and trivalent metals, respectively, have been considered.^[169] Unfortunately, the photovoltaic performances of such classes of materials remained inferior as compared with the parent perovskite, MAPbI₃. The photovoltaic performance of such systems did not excel primarily due to a wider bandgap of 2 eV and above.^[170] The truncated efficiency of these perovskites is also closely related to defect physics in the materials. The presence of deep-level defects in those ternary and double perovskites has been considered to be one of the major roadblocks against achieving high-efficiency solar cells. Understanding the origin of defects and defect passivation techniques in these systems has remained crucial for further advancement toward improving the performance of devices based on such perovskites.

4.2. Defects in Double Perovskites

Double perovskites are considered to be a stable and less-toxic alternative to $MAPbI_3$ and its derivatives. In a double-perovskite structure, the bivalent lead ion is replaced by a combination of heterovalent cation(s), leading to formation of $A_2M(I)M(III)X_6$ or

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Table 3. Different defect engineering approaches used in APbX₃-based perovskite devices.

Defect-passivation technique	Passivating agent	Target defect	Mechanism	Perovskite system	Heterojunction	J _{sc} [mA/cm²]	V _{oc} [V]	FF	PCE [%]	Ref.
Compositional engineering	Cs	lon vacancy	Filling	$FA_{0.85}MA_{0.1}Cs_{0.05}Pb1_2Br_{0.3}$	c-TiO ₂ /mp-TiO ₂ /perovskite/ Spiro-OMeTAD	22.00	1.13	0.77	19.10	[104]
	In situ PbI_2	Halide vacancy	Strain relaxation	$(FAPbI_3)_{1-x}(MAPbBr_3)_x$	SnO ₂ /perovskite/Spiro- OMeTAD	23.36	1.06	0.78	19.55	[187]
	I ₂ /IPA	Halide vacancy	Filling	MAFAPbI _{3-x} Br _x	bl-TiO ₂ /mp-TiO ₂ /perovskite/ Spiro-OMeTAD	25.00	1.10	0.80	22.10	[85]
	l ₂ /antislovent washing	Halide vacancy	Filling	MAPbI ₃	TiO ₂ /MAPbI ₃ /Spiro-OMeTAD	22.39	1.17	0.79	21.33	[114]
Inorganic Doping	Na ⁺ ,	MA vacancy	Substitutional filling	MAPbI ₃	c-TiO ₂ /mp-TiO ₂ /perovskite/ Spiro-OMeTAD	22.97	0.90	0.73	15.14	[119]
	Ag^+	MA vacancy	Substitutional filling	MAPbI ₃	c-TiO ₂ /mp-TiO ₂ /perovskite/ Spiro-OMeTAD	19.24	1.02	0.71	14.18	[119]
	Cu^+	MA vacancy	Substitutional filling	MAPbI ₃	c-TiO ₂ /mp-TiO ₂ /perovskite/ Spiro-OMeTAD	21.81	0.99	0.72	15.25	[119]
	\mathbf{K}^+	MA vacancy	Substitutional filling	MA _{0.15} FA _{0.85} Pb(I _{0.85} Br _{0.15})	c-TiO ₂ /mp-TiO ₂ /perovskite/ Spiro-OMeTAD	22.92	1.15	0.77	20.55	[122]
	Al^{3+}	MA vacancy	Substitutional filling	MAPbI ₃	poly-TPD/perovskite/PCBM/ BCP	22.40	1.10	0.77	19.10	[124]
	KI	MA and halide vacancy	Filling and immobilizing	(Cs,FA,MA) _{0.9} K _{0.1} Pb(I _{0.85} Br _{0.15}) ₃	bl-TiO ₂ /mp-TiO ₂ /perovskite/ Spiro-OMeTAD	23.20	1.17	0.79	21.50	[202]
Organic Additive	GA	lon vacancy	Vacancy filling	MAPbI _x Cl _{3-x}	TiO ₂ /perovskite/Spiro- OMeTAD	21.24	1.07	0.75	17.13	[83]
	F4TCNQ	Metallic lead	Coordinate bonding	МАРЫ₃	NiO _x /perovskite/PCBM/BCP	19.57	1.06	0.80	16.60	[157]
	MA/EtOH	Cation vacancy	Filling, Ostwald ripening	MAPbI ₃	SnO ₂ /perovskite/Spiro- OmeTAD	22.98	1.13	0.77	20.02	[81]
	IA	Cation vacancy	Substitutional filling	$MA_{1-x}IA_xPbI_3$	PTAA/perovskite/PC ₆₁ BM/ BCP	20.07	1.03	0.80	16.03	[127]
	Zinc porphyrin	Undercoordinated Pb ²⁺	Coordinate bonding	Cs,FA,MA perovskite	SnO ₂ /perovskite with YD ₂ -O- C ₈ /Spiro-OMeTAD	24.4	1.05	0.80	20.50	[203]
Lewis acid base reaction	IPFB	Undercoordinated I ⁻	Halogen bonding	MAPbI _x Cl _{3-x}	bl-TiO ₂ /mp-Al ₂ O ₃ /perovskite/ Spiro-OMeTAD	23.38	1.06	0.67	15.70	[129]
	Pyridine	Undercoordinated Pb ²⁺	Coordinate bonding	MAPbI ₃	bl-TiO ₂ /perovskite/Spiro- OMeTAD	22.00	1.15	0.73	18.50	[204]
	IDIC	Undercoordinated Pb ²⁺	Coordinate bonding	MAPbI ₃	PTAA/perovskite/IDIC/C ₆₀ / BCP	22.96	1.11	0.76	19.50	[205]
	DTA	Undercoordinated Pb ²⁺	Coordinate bonding	MAPbI _{3-x} Cl _x	PTAA/perovskite/DTA/C ₆₀ / BCP	22.50	1.17	0.81	21.45	[206]
Passivation Layer between perovskite	FABr	lon vacancy	Grain modulation	FAPbBr _{3-x} l _x	bl-TiO ₂ /mp-TiO ₂ /Spiro- OMeTAD	23.18	1.16	0.79	21.31	[139]
and HTL	PDMS	lon migration	GB passivation	МАРЫ₃	SnO ₂ /MAPbI ₃ /PDMS/CuSCN	23.9	1.02	0.78	19.04	[142]
	Fullerene derivative	Pbl ₃ ⁻ antisite (at GB)	Coordinate bonding	MAPbI ₃	NiO _x /perovskite/fullerene derivative/PCBM/Ag	22.04	1.02	0.78	17.63	[143]
	Ethylene amine capping layer	I ⁻ vacancy	Hydrogen bonding	MAPb13	TiO2/LD perovskite/3D perovskite/LD perovskite/ Spiro-OMeTAD	22.77	1.06	0.75	18.09	[140]
	Phenethyl ammonium iodide	I^- vacancy	Vacancy filling	$(FAPbI_3)_{1-x}(MAPbBr_{3-y}Cl_y)_x$	SnO ₂ /perovskite/Spiro- OMeTAD	25.04	1.18	0.77	22.98	[141]
	PEAI	I^- vacancy	Filling	$FA_{1-x}MA_xPbI_3$	SnO ₂ /perovskite/PEAI/Spiro- OMeTAD	24.90	1.16	0.81	23.56	[163]

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Table 3. Continued.



Defect-passivation technique	Passivating agent	Target defect	Mechanism	Perovskite system	Heterojunction	J _{sc} [mA/cm²]	V _{oc} [V]	FF	PCE [%]	Ref.
Passivation Layer between perovskite and ETL	QAHs (Zwitterion)	lon vacancy	Hydrogen bonding and electrostatic interaction	$FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$	PTAA/perovskite/C ₆₀ /BCP	23.70	1.14	0.78	21.00	[71]
	PTAA	lon migration	GB passivation	$MAPbI_{3-x}CI_x$	PTAA-modified PEDOT:PSS/ perovskite/PCBM	21.58	1.07	0.82	19.04	[207]
	РММА	I^- vacancy	Coordinate bonding	Cs _{0.07} Rb _{0.03} FA _{0.765} MA _{0.135} PbI _{2.55} Br _{0.45}	In-doped TiO _x /mp-TiO ₂ / perovskite/Spiro-OMeTAD	23.20	1.16	0.76	20.40	[145]
Dual layer passivation	Thioctic acid	Pb ²⁺ , Ti ⁴⁺	Coordinate bonding	MAPbI ₃	compact TiO ₂ /MAPbI ₃ -poly TA/Spiro-OMeTAD	23.48	1.14	0.76	20.40	[146]
	n-BAI	lon migration	Physical barrier	Cs _{0.07} Rb _{0.03} FA _{0.765} MA _{0.135} PbI _{2.55} Br _{0.45}	compact-mp TiO ₂ /PMM: PCBM/n-BAI/perovskite/ n-BAI/Spiro-OMeTAD	23.94	1.20	0.79	22.77	[147]
Passivation in transport layer	Defective TiO ₂	lon migration	Ionic bonding, GB passivation	$MAPbI_{3-x}Br_x$	defective TiO2/perovskite/ Spiro-OMeTAD	23.11	1.06	0.78	19.0	[144]
	TiO ₂ -Cl	lon migration	GB passivation	$FA_{0.85}MA_{0.15}PbI_{2.55}Br_{0.45}$	TiO ₂ -Cl/perovskite/Spiro- OMeTAD	21.70	1.17	0.79	20.10	[150]
	SnO ₂ -KCl	lon migration	GB passivation	(FAPbI ₃) _{0.95} (MAPbBr ₃) _{0.05}	SnO2-KCl/perovskite/Spiro- OMeTAD	24.2	1.137	0.81	22.20	[151]
	PCDTBT	lon migration	GB passivation	MAPbI ₃	TiO ₂ /PCBM/perovskite/ PCDTBT/MoO ₃	22.20	1.14	0.80	19.10	[154]
3D perovskites passivated by 2D perovskites	BA	lon migration	GB passivation	BA₂PbI₄/MAPbI₃	PTAA/perovskite/PCBM/C ₆₀ / BCP	22.49	1.11	0.78	19.56	[164]
Physical passivation	Heat	Halide vacancy, Ion migration	Strain relaxation, GB passivation	MAPbI ₃	PEDOT:PSS/perovskite/ PCBM/BCP	21.10	0.91	0.81	15.60	[74]
	VASP	lon migration	GB passivation	$FA_{0.81}MA_{0.15}PbI_{2.55}Br_{0.45}$	bl-TiO ₂ /mp-TiO ₂ /perovskite/ Spiro-OMeTAD	23.99	1.07	0.80	20.47	[158]

 $A_2M(IV)X_6.^{[171]}$ In the former class of compounds, two bivalent lead ions are replaced by one monovalent and one trivalent ion; in $A_2M(IV)X_6$, the two lead ions are replaced by a tetravalent ion and a vacancy site renaming the compound as a vacancy-ordered halide double perovskite. $^{[172,173]}$ Possible structures of a multitude of halide double-perovskite materials have been theoretically predicted. Only a few of them could however be synthesized successfully and a fewer have shown promising results for application in optoelectronic devices. In general, double perovskites are reported to possess a superior stability under ambient conditions. $^{[174]}$

4.2.1. Defect Analysis

Among vacancy-modulated double perovskites, Cs_2SnX_6 and cesium hexabromopalladate(IV) (Cs_2PdBr_6) have been reported to exhibit an enhanced stability and interesting optoelectronic properties.^[175] Cs_2NaBiI_6 -based solar cells with excellent stability and reproducibility have also been reported.^[176] Double perovskites like $Cs_2NaBiCl_6$, Cs_2KBiCl_6 , and $(CH_3NH_3)_2AgBiBr_6$ were reported to possess a wide bandgap in the 2–3 eV range.^[8,170,177] Within the group of methylammonium-based double perovskites, $(CH_3NH_3)_2SnI_6$ has been proposed to possess an optimal bandgap for solar cell applications; evidence of solar cell fabrication with the material is still absent presumably due to its inferior film quality. In a Ti(IV)-based vacancy-ordered bromide double-perovskite (Cs₂TiBr₆), a solar cell efficiency of 3.3% has been reported.^[178,179]

Optoelectronic properties of double perovskites are significantly affected by defects in the crystals. Theoretical calculations were carried out to estimate defect formation energies and identify dominant defects in double-perovskite systems. DFT calculations were used to estimate band structures and defects in the Cs₂AgBiX₆ class of double perovskites.^[180,181] The VBM of Cs₂AgBiBr₆ could be seen to provide major contributions from antibonding states of Br(4*p*) and Ag(4*d*) orbitals; Bi(6*s*) lies below the VBM with no significant contributions. The CBM, on the other hand, consists of Bi(6*p*) with minor contributions from Ag(5*p*) and Br(4*p*) orbitals. With the VBM located at **X**-point and CBM at L-point of momentum space, Cs₂AgBiBr₆ turned out to be an indirect-bandgap semiconductor.^[180,181]

Filip et al. and Xiao et al.^[180,181] in fact calculated formation energies of 20 possible intrinsic defects in $Cs_2AgBiBr_6$ system: four vacancies (V_{Cs} , V_{Ag} , V_{Bi} , and V_{Br}), four interstitials (Cs_i , $AgBi_i$, and Br_i), six cation-on-cation antisites (Cs_{Ag} , Cs_{Bi} , Ag_{Cs} , Ag_{Bi} , Bi_{Cs} , and Bi_{Ag}), three cation-on-anion antisites (Cs_{Br} , Ag_{Br} , and Bi_{Br}), and three anion-on-cation antisites (Br_{Cs} , Br_{Ag} , and





Figure 12. Calculated transition energy levels for intrinsic a) acceptor-type and b) donor-type defects in $Cs_2AgBiBr_6$. Reproduced with permission.^[181] Copyright 2016, John Wiley and Sons.

Br_{Bi}). Defect formation energies of these defects are shown in **Figure 12**. Among these defects, four vacancy defects have low formation energies, affecting optoelectronic properties of the double-perovskite. V_{Ag} is reported to possess the lowest enthalpy of formation; it hence appears as a shallow defect above VBM. The shallow nature of V_{Ag} is attributed to a strong antibonding coupling between Ag(4*d*) and Br(4*p*) orbitals, which push the VBM to a higher energy level turning the V_{Ag} level to become further shallow. V_{Bi} on the other hand exhibits a deep transition level. Among the 12 antisites, Ag_{Bi} and Bi_{Ag} have relatively low formation energies. Other intrinsic defects with high formation energies do not influence the optical and electrical properties of $Cs_2AgBiBr_6$.

Xu et al. and Volonakis et al. independently investigated Cs₂AgInX₆ compounds using DFT calculations.^[182,183] In Figure 13, the electronic band structures of such double perovskites have been presented as obtained from first-principle calculations along with the projected DOS. Unlike Ag-Bi systems, Ag-In-based double perovskites exhibit a direct bandgap. This is due to the fact that the VBM of Cs₂AgInX₆ (X: Cl, Br) has a minimal contribution from In(5s) orbitals and is mainly formed by the hybridization between Ag(4d) and X(p) orbitals. They estimated that Ag_i and V_{Br} possessed the lowest defect formation energy and acted as shallow donors enforcing intrinsic n-type conductivity in Cs2AgInBr6. Overall, although lead-free-halide double perovskites have emerged as promising materials for application in various optoelectronic devices, the performance of double-perovskite-based devices is far below their theoretically predicted values. Understanding the origin of defects and suitable defect passivation techniques is hence crucial for further advancement toward improving the performance of such perovskite-based devices.[182,183]

4.2.2. Defect Passivation

Luo et al. have reported that doping of Cs₂AgInCl₆ with sodium ions partly prevents the forbidden transitions in the double perovskite and thereby improves the PL quantum yield (PLQY) to \approx 80% as compared with the QY of 0.1% in pristine Cs₂AgInCl₆.^[184] The pristine material exhibits a broad-band white light emission. As per their work, Na⁺ doping alters the orbital nature of trapped excitons, breaking the partly forbidden transitions; this reduces electronic dimensionality, leading to radiative recombination of self-trapped excitons and improving the PL in doped samples.^[184]

Using first-principle calculations, Xu et al. have investigated the formation of deep-level defect states arising from grain



Figure 13. a) Comparison of HSE + SOC calculated electronic band structures and orbital-projected DOS for Cs₂AgBiBr₆, Cs₂AgBiCl₆, Cs₂AgBiCl₆, and Cs₂AgInCl₆ and b) the projected DOS of s, *p*, *d* orbitals which are colored in green, red, and blue, respectively. Reproduced with permission.^[182] Copyright 2017, American Chemical Society.



boundaries in Cs₂AgInCl₆ and Cs₂AgBiCl₆.^[185] The electronic band structure at a particular GB namely $\Sigma 5(310)$ shows the presence of deep-level defect states at the grain boundaries which can adversely affect the performance of double-perovskite-based devices. They have observed that through doping of $Cs_2AgInCl_6$ with Cl_i (chloride interstitial defect) and In_{Ag} (indium at silver sites) defects, deep-level states arising from grain boundaries can be passivated through modification of electronic structures (Figure 14a). With a schematic diagram (Figure 14b), they have shown that upon Cl_i doping, the S1 GB defect states move closer to VBM. Similarly the InAg antibonding states push S1 and S2 states closer to CBM. The combined effect of Cl_i and In_{Ag} defect segregation at the grain boundaries removes the defect states from the band gap. Similar observation was reported on Cs2AgBiCl6 crystals upon Cl_i doping. Their study indicated that spontaneous segregation of defects at grain boundaries could be used as a method to eliminate deep-level defect states.^[185]

Nandha et al. have reported Mn^{2+} -induced luminescence from $Cs_2AgInCl_6$. This material is absorbed in the UV region and transfers the energy to *d*-orbital electrons of manganese ions occupying the lattice sites.^[186] De-excitation from the Mn(d) levels leads to PL in the red region. In a somewhat similar report, Chen et al. have reported Yb³⁺-induced near-infrared emission in addition to the trap-state visible region PL in Cs_2AgBiX_6 .^[187] They have found that doping of Yb³⁺ can be useful to remove the deep-level defect states situated within the bandgap, resulting in an increase in the PLQY. By controlling the dopant concentration, they have tuned the emission profile and dynamics of photon relaxation (Figure 15). Furthermore, they have reported that their synthesis approach is also suitable to yield dopant-induced luminescence from Cs₂AgBiX₆. In another article, Ce³⁺ doping in Cs₂SnI₆, which is a vacancy-modulated double perovskite, has resulted in improving PL emission. Here, the Ce³⁺ ions have introduced (Ce³⁺Sn⁴⁺+V_{Cl}) and (Sn²⁺Sn⁴⁺+V_{Cl}) defects, promoting radiative recombination pathways and thereby increasing the PL intensity.^[188]

Tran et al. have shown that doping of Cs₂AgInCl₆ with antimony ions converts direct bandgap of pristine Cs₂AgInCl₆ to an indirect one. They have reported that the CBM, which was initially composed of s-orbitals, forms with p-orbitals upon an increase in antimony content; this in turn decreases the bandgap and results in an indirect-bandgap semiconductor.^[189] On the other hand, Slavney et al. have reported band-edge reconstruction in $C_{s_2}A_gBiBr_6$ by doping with tantalum ions (T1⁺). They have observed that Tl⁺ ions at lower doping concentrations reduce the bandgap of the material by $\approx 0.6 \text{ eV}$; at higher contents of Tl^+ ions, the nature of bandgap turns to a direct one. $^{[190]}$ Similarly, the report of Karmakar et al. on Cu2+-doped Cs₂SbAgCl₆ double perovskites has evidenced a significant reduction in the bandgap (from 2.6 to 1.0 eV).^[191] They have inferred that the incorporation $3d^9$ orbitals of Cu²⁺ near the VBM of Cs₂SbAgCl₆ has led to the reduction of bandgap while retaining the 3D structure of the double perovskite.^{[191}

The elimination of ion migration in $Cs_2AgBiBr_6$ polycrystalline films has been reported through deposition of BiOBr



Figure 14. a) Calculated band structures of Cs₂AgInCl₆ with Σ 5(310) (representation of a particular GB) GB after Cl_i and In_{Ag} + Cl_i incorporation and b) schematic diagram of the Cl_i and In_{Ag} + Cl_i incorporation at the GB in Cs₂AgInCl₆ to eliminate the deep defect states within the bandgap. Reproduced with permission.^[185] Copyright 2019, John Wiley and Sons.





Figure 15. a) Absorption and PL spectra of Yb-doped Cs_2AgBiX_6 (X = Cl⁻, Br⁻) and b) Mn-doped $Cs_2AgBiCl_6$ double-perovskite nanocrystals. Reproduced with permission.^[187] Copyright 2019, American Chemical Society.

passivating layer. Due to a fair degree of lattice matching with the double perovskite, the BiOBr layer aided defect passivation, inhibited ionmigration, and hence improved X-ray detection ability of the double perovskite.^[192]

Till date, Cs₂AgBiBr₆ has been one of the most-successfully used double perovskites in the fabrication of thin-film solar cells. A poor morphology of Cs₂AgBiBr₆ films with large crystallites and pinholes has been stated to be one of the major reasons toward resulting in ill-performed devices. Recently, Wu and coworkers have reported an antisolvent and postannealing treatment of Cs₂AgBiBr₆ that can arguably enhance the crystal quality and PCE of the solar cells.^[193] Another facile strategy has been reported of late for passivating the defects by introducing an N719 dye interlayer in a solar cell architecture.^[194]

4.3. Defects in Ternary Halide Perovskites (Triple Perovskites)

An optimistic avenue to achieve lead-free halide perovskites can also be imagined in a structure like A3M2X9 with layers of metalhalide bioctahedral being connected through a monovalent cation. As stated earlier, the ternary halide perovskites, which are frequently termed defect-ordered perovskites, have been considered through a combinatorial approach of a bivalentmetal-based AMX₃ perovskite; in A₃M₂X₉, a section of the metal site (*M*) is swapped by vacancies.^[195] Structures like A₃M₂X₉ with metal-halide MX₆ octahedral layers have hence been envisaged considering Bi³⁺ or Sb³⁺ in the metal site and methylammonium (MA⁺), formamidinium (FA⁺), cyclohexyl ammonium, imidazolium, K^+ , Rb^+ , or NH_4^+ as the singly protonated cation (A-site) which plug the voids between the layers.^[8,196] Depending upon the growth condition, this type of perovskite can result either in 1) a 0D hexagonal close-packed structure having isolated face-sharing MX₆ octahedra instead of a 3D corner-sharing octahedra or 2) a 2D defect perovskite with corrugated double layers of corner-sharing MX₆ octahedra. The advantages of these lead-free perovskites are their low toxicity and a better air stability than the prototype CH₃NH₃PbI₃. However, device performance of perovskites has not shone mostly due to a large bandgap of the order of 2 eV or more, resulting in a low efficiency (η) as per the Shockley–Queisser limit.^[195,197] Also, due to an absence of a 3D framework through corner-shared PbI6 octahedra, carrier mobility in these perovskites is also low, resulting in a reduced efficiency in devices based on such 0D systems. The abovementioned issues have recently been addressed through band engineering of the materials. It remains important to gather information about bulk and interfacial defects which unavoidably form during the band engineering and also during film formation toward device fabrication. Defect states having energies outside the gap do not in general pose a serious concern in device performance; deep-level defects existing inside the bandgap, on the other hand, adversely affect the materials' optoelectronic properties as the defect sites can act as trapping or recombination centers hindering efficient carrier conduction. Identification and more importantly passivation of these defects in A3M2X9 perovskites are hence enormously essential to work toward increasing η in A₃M₂X₉-based solar cells.^[32,56,198]

4.3.1. Defect Analysis

The most popular members of this series can be classified as bismuth-based and antimony-based perovskites with methylammonium or cesium at the A-site: $(CH_3NH_3)_3Bi_2I_9$, $Cs_3Bi_2I_9$, $(CH_3NH_3)_3Sb_2I_9$, and $Cs_3Sb_2I_9$. In general, the singly protonated cation $(CH_3NH_3^+ \text{ or } Cs^+)$ has little impact on determining the band edges, while they can participate in creating deep- or shallow-levels traps in the material.^[56] As there are few reports on determination of defect states in this class of perovskite, we have made some discussion in this respect.

First-Principle Calculations: First-principle calculations have been reported as an interesting approach to obtain insights into defect states in the $A_3B_2X_9$ perovskite system. Although mathematical calculations for MA-based ternary perovskite systems are still unavailable in the literature, some valuable information about defect states in cesium-based perovskite could be found. Ghosh et al. have provided first-principle calculations in Cs₃Bi₂I₉ and observed the presence of deep-level defect states in the material.^[56] They have classified possible point defects broadly into two types: acceptor like and donor like. By



considering different stoichiometries of the compound, they have inferred that the occurrence of defect states depends on the growth condition or stoichiometry of the precursors. While acceptor-like defects originate due to cation vacancies (V_{Cs} , V_{Bi}), iodine interstitials (I_i), Cs on Bi substitutions (Cs_{Bi}), and antisite substitutions, specifically iodide on cation (I_{Cs} , I_{Bi}), donor-like defects originate from iodine vacancies (V_I), cation interstitials (Cs_i , Bi_i), Bi-on-Cs substitutions (Bi_{Cs}), and cation-on-iodide antisite substitutions (Cs_I , Bi_I). Depending on the stoichiometry of the precursors, that is the growth condition, different defects prevail and become responsible for poor photovoltaic performance as well (**Figure 16**a,b).

In their work, Saparov et al. have also carried out band structure calculations in the Cs₃Sb₂I₉ system.^[199] In a similar fashion, they have considered different growth conditions by varying the precursor stoichiometry and determined formation energies of different defect states (Figure 16c,d). The possible defects in Cs₃Sb₂I₉ were found to be cation vacancies (V_{Cs}, V_{Sb}), iodine interstitials (I_i), Cs-on-Sb substitutions (Cs_{Sb}), and antisite substitutions, namely iodide on cation (I_{Cs}, I_{Sb}), iodine vacancies (V_I), cation interstitials (C_{si}, S_{Bi}), Sb-on-Cs substitutions (Sb_{Cs}), and cation-on-iodide antisite substitutions (Cs_I, Sb_I).

First-principle calculations in determining defect states in methylammonium-based ternary perovskite systems are still inadequate, presumably due to the complexity of the structure.^[56]

Experimental Evidences: As such, there is no clear experimental evidence to probe the defect states exactly in an A3B2X9 perovskites. Our group has made an endeavor through scanning tunneling spectroscopy (STS) in probing the presence of defect states in a ternary halide perovskite.^[32] We have studied the role of defect states on the band edges of $A_3Bi_2I_9$ (A = Cs⁺ and CH₃NH₃⁺). A range of different precursor stoichiometries were considered to achieve different reaction environments. Depending on the growth condition, different types of defects could be seen to form that affect the band energies of the materials. The band edges were determined from differential tunnel conductance (dI/dV) spectra (Figure 17a), which have a correspondence to the DOS of the material under study. The STS results have shown that the Fermi energy of the materials was always closer to the VBM than the CBM, showing a p-type nature of the perovskites, as obtained from a large number of measurements and drawn of energy-level histograms (Figure 17b). A nonintrinsic nature of the perovskite semiconductor, even when formed with stoichiometric precursors, implies the presence of point defects in such materials. Theoretical calculations have also inferred the presence of possible point defects: the defects were classified into acceptor like and donor like, as also described in the previous section. The STS studies evidenced a p-type nature of conductivity in the perovskite material irrespective of the compound being formed in a Bil₃-rich or a CsI-rich (or a CH₃NH₃I-rich) environment



Figure 16. Transition energy levels of intrinsic a) donor-type and b) acceptor-type defects. c) GGA-calculated transition energy levels of the acceptor-(blue lines) and donor- (red lines) level formation energies of intrinsic point defects and d) chemical potentials at different growth conditions (I rich/Sb poor, moderate, and I poor/Sb rich, respectively) in $Cs_3Sb_2I_9$ perovskite. Reproduced with permission.^[56] Copyright 2017. American Chemical Society. Reproduced with permission.^[199] Copyright 2014. American Chemical Society.







Figure 17. a) Typical dI/dV spectrum and b) the respective histogram of CB and VB energies of stoichiometric (1:1) Cs₃Bi₂I₉ perovskite thin films, c) band positions of Cs₃Bi₂I₉ formed with different stoichiometric ratios of the precursors, namely CsI and BiI₃, and d) Band positions of MA₃Bi₂I₉ formed with different stoichiometric ratios of the precursors, namely MAI and BiI₃. Inset of (a) shows the topography of the stoichiometric Cs₃Bi₂I₉ perovskite thin film. Reproduced with permission.^[32] Copyright 2019, Elsevier.

(Figure 17c). Interestingly, a lowering of the bandgap was achieved in $Cs_3Bi_2I_9$ formed with a CsI-rich condition, implying the formation of Cs_{Bi} vacancies in addition to other acceptor-like vacancies, such as I_{Bi} and V_{Bi} with formation energies being a little higher than that of Cs_{Bi} in the perovskites. With the support of theoretical calculations, we could also confirm the presence of V_I defects in the perovskite formed in a BiI₃-rich condition. In the methylammonium-based perovskite, $(CH_3NH_3)_3Bi_2I_9$, the bandgap did not respond upon a variation of precursor stoichiometry (Figure 17d); it has therefore been concluded that the defects present in methylammonium-based perovskites (MA_3B_2X_9) have shallow energy levels.

4.3.2. Defect Passivation

Due to the deep-level nature of defects in a system like $A_3Bi_2X_9$, defect passivation is naturally extremely important. An efficient manner of defect passivation is however sparse. Among the few available reports, the research group of Matthews has provided a route of deep-level defect suppression in the $Cs_3Bi_2I_9$ system using excess BiI_3 in the precursor solution.^[198] They have observed an improvement in the photovoltaic parameters which have been correlated with the passivation of intrinsic defects or some structural disorders. In support of their inference, they have characterized $Cs_3Bi_2I_9$ for PL and cathodoluminescence (CL) spectroscopies (**Figure 18**a). Both the spectroscopic results suggested an enhancement in the emission intensity with the addition of excess BiI₃ in the precursor, suppressing the formation of secondary phases (Figure 18b). They have also confirmed such conclusions from transient absorption (TA) spectroscopy (Figure 18c) and carrier decay dynamics (Figure 18d). The enhancement of PL intensity was hence correlated with the passivation of trap states which were present in $Cs_3Bi_2I_9$ and acted as nonradiative channels for decay of carriers.

In A₃M₂X₉ lead-free perovskite systems, Cl passivation has been reported to be an effective avenue to boost the performance of LEDs and solar cells based on such perovskites.^[200] In our research group, we have introduced a new route of defect passivation by incorporating chloride in the MA3Sb2I9 perovskite system.^[80] Apart from defect passivation, a phase transformation could be observed to have occurred in MA3Sb2I9 during the transformation from a 0D dimer phase to a 2D-layered phase upon chloride incorporation. STS studies suggested a major change in band energies due to the phase transformation process. Along with defect passivation, we have also observed a contracting nature of the local surface potential distribution as probed through KPFM (Figure 19a). With local conductivity measurement by c-AFM, we could infer that the conductivity of the antimony halide perovskite system increased upon the passivation of defects upon chlorine incorporation (Figure 19b).





Figure 18. a) Gaussian fitting of CL spectra of $Cs_3Bi_2I_9$ thin films at different electron beam currents (I_b), b) power-law fits of CL peak area against different electron beam powers, c) TA spectra of $Cs_3Bi_2I_9$ thin films for different time delays under 400 nm excitation, and d) carrier decay dynamics of the same at 493 nm. Reproduced with permission.^[198] Copyright 2018, American Chemical Society.



Figure 19. a) Contact potential images, distribution of CPD, and average surface work function of MA₃Sb₂Cl_xI_{9-x} with a range of chlorine-to-iodine (Cl/I) ratios. b) Conductivity mapping, distribution of current at 1.0 V, and a comparison between root mean square roughness (from AFM topographies) and average current of MA₃Sb₂Cl_xI_{9-x} with a range of chlorine-to-iodine (Cl/I) ratios. Reproduced with permission.^[80] Copyright 2019, American Chemical Society.

 Table 4. Major defects and passivating agents used for defect engineering in perovskites beyond ABX₃.

Perovskite	Major defects	Passivating agents	Ref.
Cs ₂ AgBiBr ₆	$\begin{array}{c} V_{Cs}, V_{Ag}, V_{Bi}, V_{Br}, Cs_i, Ag_i, \\ Bi_i, Br_i, Cs_{Ag}, Cs_{Bi}, Ag_{Cs}, Ag_{Bi}, \\ Bi_{Cs}, Bi_{Ag}, Cs_{Br}, Ag_{Br}, Bi_{Br}, \\ Br_{Cs}, Br_{Ag}, and Br_{Bi}. \end{array}$	Mn ²⁺ Yb ²⁺ doping	[180,181,186, 188,190–192]
(MA) ₂ AgBiBr ₆	No report	_	-
Cs_2NaBil_6	No report	_	-
Cs_2KBiCl_6	No report	_	-
$Cs_2NaBiCl_6$	No report	_	-
Cs ₂ AgInCl ₆	$\begin{array}{l} V_{Cs},V_{Ag},V_{In},V_{Cl},Cs_{i},Ag_{i,}\\ In_{i},Br_{i},Cs_{Ag},Cs_{In},Ag_{Cs},Ag_{In},\\ In_{Cs},In_{Ag},Cs_{Cl},Ag_{Cl},In_{Br},\\ Cl_{Cs},Cl_{Ag},andCl_{In}. \end{array}$	Na ⁺ , Mn ²⁺ doping, Cl incorporation	[182,183]
Cs_2Snl_6	$\begin{array}{c} V_{Cs}, \ V_{Sn}, \ V_{I}, \ Cs_{i}, \ Sn_{i}, \ I_{i}, \ Cs_{Sn}, \\ Sn_{Cs}, \ Cs_{I}, \ Sn_{I}, \ I_{Cs}, \ I_{Sn} \end{array}$	No report	[208]
Cs_2TiBr_6	$\begin{array}{c} V_{Cs}, \ V_{Ti}, \ V_{Br}, \ Cs_i, \ Ti_i, \ Br_i, \ Cs_{Br}, \\ Ti_{Cs}, \ Cs_l, \ Ti_l, \ Br_{Cs}, \ I_{Ti} \end{array}$	l incorporation	[179]
$Cs_3Bi_2I_9$	Cs_{Bi} , I_{Bi} , V_{Bi} , V_{I}	Excess Bil ₃	[56,198]
$Cs_3Sb_2I_9$	$\begin{array}{l} V_{Cs}, \ V_{Sb}, \ I_{i}, \ Cs_{Sb}, \ Cs_{i}, \ Cs_{l}, \\ Sb_{l}, \ I_{Cs}, \ I_{Sb}, \ Sb_{Cs}, \ S_{Bi} \end{array}$	Cl incorporation	[80]
$MA_3Sb_2I_9$	No report	-	-
MA ₃ Bi ₂ I ₉	No report	_	-

The defect landscape and passivating agents used for defect engineering in perovskites beyond ABX₃ are shown in **Table 4**.

5. Conclusion and Future Outlook

Hybrid halide perovskites offer enormous potential toward the development of next-generation solar cells. Though an outstanding progress has been witnessed over the past decade in improving the efficiency of such perovskite solar cells, there are still some gaps toward the commercialization of technology. The prevailing challenges of perovskite solar cells in terms of device performance and long-term stability are fundamentally governed by defect physics; hence, defect engineering has now become a crucial aspect in optimizing the performance of perovskite solar cells. In this Review, we have discussed about the ensemble of defects, their possible origins, a host of defect analysis techniques, and effective methods to passivate the defects in prototype solar cells based on methylammonium lead halide and its derivatives. In our discussion, we have also highlighted the limitations of existing methods while investigating the origin of defects.

In this context, the recently developed "super-cell" approach has been considered to be an effective method toward addressing the limitations of first-principle calculations. Considering some recent developments, we have identified some cutting-edge experimental techniques in probing the defects at the local scale and the defects' function in restraining device performance and prompting device degradation. These defects have been found to promote nonradiative recombination in perovskite solar cells that

in turn limit V_{OC}, amplify hysteresis phenomena, and hamper carrier transport besides affecting long-term device stability. A combination of different techniques, such as scanning probe microscopy, transient measurements, and ultrafast carrier dynamics at the nanoscale have been found to be appropriate in investigating defect physics in terms of their nature, concentration, and local response. Based on the understanding, we have considered passivation of defects as the next proficient strategy; we have expanded our discussion on different approaches to passivate the defects in the bulk, on the surface, and at grains and grain boundaries. We have summarized some pioneering material-engineering approaches to passivate the defects and thoroughly discussed their role in understanding the nature, density, and distribution of such defects in perovskite materials and devices. A detailed discussion on the effectiveness of some experimental approaches such as compositional tuning, engineering of charge transport layers, and introduction of interfaces in reducing defect-assisted nonradiative recombination in solar cells to improve the V_{OC} of the devices has also been presented.

We expect that such materials and device engineering can be effective in suppressing the ion migration, reducing photocurrent hysteresis, and improving the long-term device stability. Furthermore, we believe that interfacial engineering by manipulating the surfaces and GBs with passivating agents can be highly effective in reducing the recombination centers and can improve the carrier transport process and also enhance the device performance. In this context, we have argued the necessity of developing a proper band alignment between charge transport layers and the perovskite absorber as a smart approach to minimize the defect density and promote facile charge transport. A few new routes, such as fabrication of single-crystalline thin films with fewer defects and grain boundaries, design of new molecules as passivation layers, and new charge transport layers to fully passivate the defects on the surface and/or at GBs, have also been discussed in this Review. Our discussion has rightfully addressed how the study of defects in ABX3 and beyond the prototype perovskite is essential for the commercialization of perovskite solar cells. On a broader note, it is expected that the solar cell efficiency would further increase toward the theoretically predicted limit upon addressing the prevailing issues with defects through defect engineering and post-treatment techniques.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

defect engineering, defect passivation, device efficiencies, defect states, hybrid halide perovskites, origin of defects

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