Review

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Cs2AgBiBr6 and Cs2TiBr6 Perovskite Solar Cells: The Challenges and Research Roadmap for Power Conversion Efficiency Improvement

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Review

$Cs_2AgBiBr_6$ and Cs_2TiBr_6 Perovskite Solar Cells: The Challenges and Research Roadmap for Power Conversion Efficiency Improvement

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Abstract: The stability issues in the widely known organic inorganic halide perovskite, $CH_3NH_3PbI_3$, leads to the development of alternative halide double perovskite materials which get great attention in recent times. Although the stability issue seems promising, both materials and device performance of these photovoltaic materials remain inferior and challenging for improvements. Furthermore, the power conversion efficiency of single junction organic inorganic halide perovskite is now 24.2% and 29.15% for textured monolithic perovskite/silicon tandem solar cell, but for all-inorganic halide perovskite solar cell is 7.11% and halide double perovskite solar cells based on $Cs_2AgBiBr_6$ and Cs_2TiBr_6 is 2.50% and 3.3%, respectively, which is far less than 24.2% and 29.15%, respectively. This creates big question and concern that can both all-inorganic halide perovskite solar cell and halide double perovskites solar cells really be an acceptable alternatives to replace organic inorganic halide perovskite solar cells or lead based perovskite solar cells in the market in order to realize the practical applications? Not only this concern, but also there are many other big challenges facing by halide double perovskite solar cells. Such big challenges include: a) geometric constraints and limited integration with interfacial materials, b) dynamic disorder and a wide bandgap and localized conduction band caused by cubic unit cell which restrains the interactions of orbitals, c) high processing temperature which may limit on the diverse applications, d) low electronic dimensionality making them less appropriate for single junction solar cell purpose and etc. Moreover, origin of electronic and optical properties such as the polarizability, the presence of molecular dipoles and their influence on the dynamics of the photo-excitations in the halide double perovskites remains unlock concern that need to be elucidated. Now, another big question is how to develop overcoming mechanisms for such challenges. Can we really overcome these current limitations faced by halide double perovskites so that we use them for commercialization? This research roadmap for performance improvement is suggested focusing on: materials surface and bulk engineering, bandgap engineering, interfacial engineering, composition engineering, doping engineering, device architectural engineering, polar and domain order engineering. This was the reason that this review was developed in order to forward great contributions to the readers and commercial ventures.

Keywords: lead free; all inorganic; halide double perovskite; performance improvement

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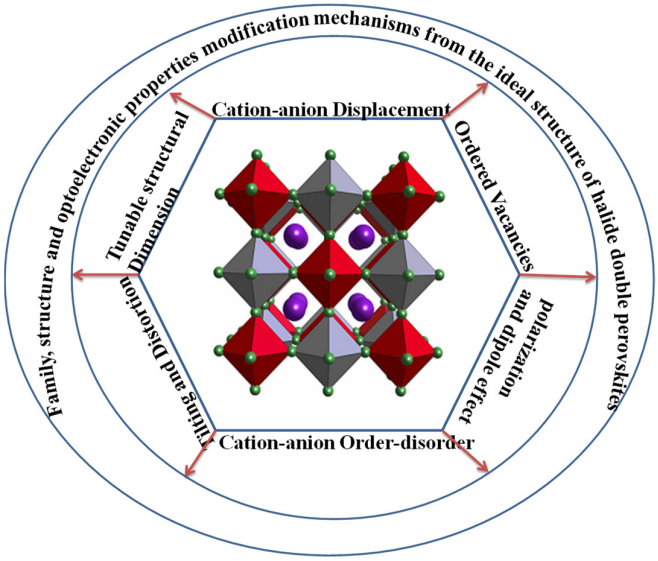
Graphical Abstract



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1. Background

A definitive objective of materials utilized in optoelectronic applications ought to be founded on the "triple-E" terms: financially **e**conomical, vitality **e**ffective and naturally **e**fficient. In spite of their very great execution in lead halide perovskite based solar cells with efficiencies reached 24.2% and the rising application for lasers [1], light-radiating diodes (LEDs) [2], and field-impact light-producing transistors (FETs) [3], organic–inorganic lead halide perovskites experience the ill effects of high substance of lethal, contaminating, and bioaccumulative Pb, which may in the end hamper their commercialization. Progressively, It turn out to be accordingly of essential significance to consider and create alternative classes of lead free halide double perovskites for various optoelectronic applications [4]. The need of creating practical advances dependent on ecologically neighborly, earth-inexhaustible, and financially savvy materials normally drives the consideration toward the change metals, where especially appealing metals (e.g., Fe^{2+}, Cu^{2+}, Zn^{2+}) and post transition elements [5,6]. For example, Tin [7–9], Rubidium [10,11], Indium-Silver [12,13], Titanium [14], Bismuth and Silver-Bismuth [12,15–18] and Copper [19] based perovskites have been found as potential choices to toxic perovskites. Thanks to their rich science, their utilization may tremendously broaden engineered courses of new halide double perovskites for photovoltaic and light-radiating applications enhancing the tunability of the material. Moreover, the discovery of lead-free double perovskites provides a feasible way of searching for air-stable and environmentally benign solar cell absorbers [6,19–25]. Since the 1970s, a large number of double perovskites (which are well known as elpasolites) with nominal chemical compositions of $A_2M^IM^{III}X_6$ (A and M^I = Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+, etc., M^{III} = Bi^{3+}, Al^{3+}, Ln^{3+}, Ga^{3+}, Fe^{3+}, etc., and X = F, Cl, Br, or I) have been initially reported as ferroelectric materials [26,27]. However, the **Lead and Tin free** all-inorganic halide double perovskite solar cell power conversion efficiency is far smaller than the power conversion efficiency (PCE) of lead based perovskite solar cells. The reason why the **Lead and Tin free** all-inorganic halide double perovskites' PCE improvement is too slow compared to lead halide perovskites PCE become great concern and active research direction for the halide double perovskite scientific community. In conjunction with the advancement of halide double perovskite solar cells, interesting concepts covering cationic exchange, doping and alloying for engineering the electronic structure of double perovskites [28], and its crystal structure, preparation approaches, physicochemical properties and material various applications [29], [6,24] various strategies such as hetero-substitution of Pb to form quaternary halide double perovskites [5], and a strategy for achieving small bandgaps in this family of materials [30]. Moreover, the PCE of single junction lead based perovskite is now 24.2% [31], 25.2% [32] and 29.15% [33] for textured monolithic perovskite/silicon tandem solar cell, but the record for lead free all inorganic cesium tin-germanium triiodide ($CsSn_{0.5}Ge_{0.5}I_3$) solid-solution perovskite is 7.11% [34]. According to the simulation results reported, $CsSn_{0.5}Ge0.5I_3$ perovskite material can have power conversion efficiency of 18.79% [35] and 24.63% [36]. Furthermore, $CsSn_{0.5}Ge_{0.5}I_3$/$FASnI_3$ device architecture is reported with simulated power conversion efficiency of 31.58% [37]. This indicates that $CsSn_{0.5}Ge_{0.5}I_3$/$FASnI_3$ device is promising device for high performance lead free solar cells.

This efficiency can be achieved if encapsulation mechanisms, fabrication procedures and material parameters such as defect density, layer thickness, operating temperature, electron affinity potential energy are well optimized during experiment. Moreover, tin based perovskite solar cells have promising efficiency next to lead based perovskite solar cells, devices made of Tin based perovskite materials exhibit insufficient stability [38] and it contains intrinsically deep defects that are detrimental to the perovskite solar cell performance [39]. Even the most stable $CsSn_{0.5}Ge_{0.5}I_3$ based perovskite solar cell showed 10% decay in efficiency after 500 h of con- tinuous operation in N_2 atmosphere under one-sun illumination [34]. Hence, to overcome the toxicity of lead and insufficient stability of Tin, efforts to find alternative perovskite materials, which are earth-abundant, non-toxic, stable and biocompatible, are still in progress.

Based on these needs, lead and tin free all-inorganic solar cells such as $Cs_2AgBiBr_6$ and Cs_2TiBr_6 have been reported recently. The record for $Cs_2AgBiBr_6$, and Cs_2TiBr_6 lead and tin free all-inorganic halide double perovskite solar cell are 2.5% [40] (current report is 2.81% [41] with photoelectronic conversion efficiency of hydrogenated $Cs_2AgBiBr_6$ perovskite solar cell of 6.37% [42]) and 3.3% [43],

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respectively, which are far less than 24.2% for single junction lead based halide perovskite solar cells and 29.15% for tandom solar cell. Consequently, the progress is yet too slow to reach the lead halide perovskite solar cells. From theoretical perspective, simulation results reported that Cs_2TiBr_6 has achieved 11.49 % power conversion efficiency [44]. This is promising to manufacture practical lead free double halide perovskite solar cell. More recently, an Au/CuSbS2/Cs_2TiBr_6/CdS/TCO configuration has achieved power conversion efficiency of 23.77% as reported by simulated results [45]. This is again more promising result in this field. Unless the real and bottleneck challenges and bottleneck solutions are clearly identified to be solved, $Cs_2AgBiBr_6$ and Cs_2TiBr_6 based halide double perovskite solar cell will not be able to be first alternative solar cell to replace the lead halide perovskite solar cells. Thus, this review article is designed to identify the challenges and possible solutions for power conversion efficiency improvement of halide double perovskite solar cells that will be considered as research roadmap for performance improvements in this field. Hence, this is a comprehensive review that concisely reviews the modification strategies from $CH_3NH_3PbI_3$ into many halide double perovskites materials, origin of electronic and optical properties variations, key challenges and areas of research for possible solutions and performance improvement strategies of both Lead and Tin free all-inorganic halide double perovskite solar cells. Moreover, this will provide a new perspective and research roadmap for performance improvement to the scientific community and research industries.

2. Modification Strategies from $CH_3NH_3PbI_3$ into Many Halide Double Perovskites

Solar cell devices made of organic-inorganic lead halide perovskite material ($CH_3NH_3PbI_3$) has been reported in 2009 with cell efficiency of 3.81% [46], indicating that $CH_3NH_3PbI_3$ with current efficiency of 24.2% [31] achieved in 2019 is promising if the device made of it is further optimized continuously. Gradually, modification of $CH_3NH_3PbI_3$ has been done at three sites as shown in Scheme 1: [47] strategy 1) halogen atoms like chlorine, bromine and combination of all these halogens [48–51], strategy 2) organic part [52–55] and Strategy 3) at the metal Pb site such as Ge [56], bismuth or antimony and noble metals [57] [12,18,19,58–61]resulting many derivatives of $CH_3NH_3PbI_3$ materials classified as organic-inorganic perovskites, fully inorganic perovskites and halide double perovskites etc. All these modifications are the subject of this section and classified as cation displacement at A and B site, anion displacement at X-site. Furthermore, all these cation and anion modifications as well as the tunable structural dimensions, cation-anion order disorder, distortions and tilting of the octahedral unit, BX_6, from the ideal structure are collectively considered as the origin of diversity in materials structure, dimension and optoelectronic properties**.** In addition, the low stability and Pb toxicity challenges in $CH_3NH_3PbI_3$ led to find other alternatively stable and nontoxic halide perovskites materials, which lead to the discovery of halide double perovskites materials, which are the focus of this review.

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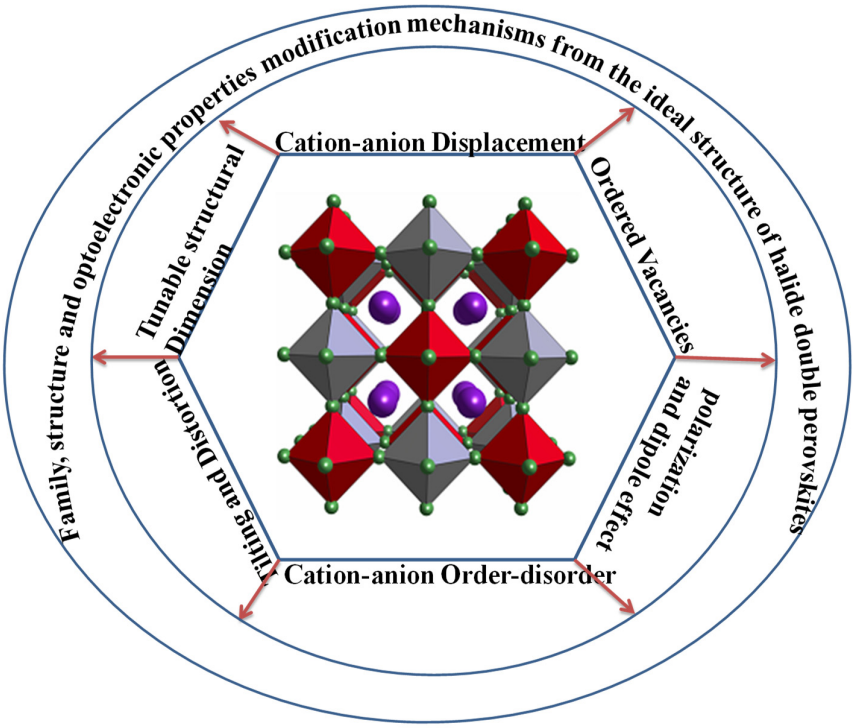

Scheme 1. Halide double perovskite family, structure and optoelectric properties modification mechanisms.

3. Origin of Electronic and Optical Property Variations

In addition to the structural variations, optoelectronic properties such as absorption, electron-hole diffusion length, carrier life time, carrier mobility, charge carrier dynamics, electronic structure such as band structure and density of state, effective mass of electron, thermal properties and other electrical properties such as ferroelectric, pyroelelctric and piezoelectric properties are the main materials properties that every one want to deal with for further energy application of materials. Recently, the field of organic-inorganic halide hybrid perovskite become revolutionize the field of photovoltaics. Moreovere, modifying the halide perovskites gives new halide double perovskites for which the stated properties are not well studied. Thus, understanding the origin of these optoelectronic property variations would be of great interest for the development of halide double perovskite materials's performance. In this section, molecular dipoles, tilting of octahedron and taransition metal cation size and its oxidation states on photo-excitation, band structure, photoluminescence, and other optoelelctric properties.

4.1. Effect of Polarizability and Molecular Dipoles on the Dynamics of the Photo-Excitations

Regardless of fast improvements in both photovoltaic and light producing gadget execution, the comprehension of the optoelectronic properties of halide double perovskites is as yet fragmented. Specifically, the polarizability of the material, the nearness of sub-atomic dipoles, and their impact on the dynamics of the photo-excitations remains an open issue to be cleared up. From now on, the imperative subject of discussion has been to do with the seemingly perpetual polarization of the perovskite under connected electric fields [62,63]. This impact shows itself as a huge hysteresis in the deliberate flow – voltage bends of perovskite sun oriented cells and LEDs in planar heterojunciton designs, contingent upon the contact materials used [62,64,65]. The people group has been attempting to comprehend whether the watched polarization is because of the relocation of versatile charged imperfections, atomic dipole arrangement, or to a ferroelectric reaction. The vast majority of the ongoing work underpins the speculation that particle migration [62,65,66], ought to rule any ferroelectric conduct at room temperature [67]. Leijtens et.al [*68*]. explored the impact of a connected

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outer electric field on the photograph energized types of $CH_3NH_3PbI_3$ thin movies, both at room temperature and at low temperature, by checking the photoluminescence (PL) yield and PL rots. At room temperature these creators discovered proof for electric field – incited decrease of radiative bimolecular bearer recombination together with movement of charged imperfections that influences the non-radiative rot rate of the photoexcited species. This has been allotted to field incited arrangement of the atomic dipoles, which diminishes the vibrational opportunity of the cross section and the related nearby screening, and henceforth results in a more grounded electron gap interaction [68].

4.2. Effects of Tilting on the Band Structure and Electron-Hole Transport

Diverse degrees of tilting of the octahedra offer ascent to various precious crysyal fields, which result in various electronic and optical properties. The degrees of tilting may influence the band structure, electron and gap transport properties, photoluminescence, and dielectric conduct.

5. Energy Applications of Halide Double Perovskites

The key point researchers deal with materials property is to obtain promising materials property for certain promising applications [21]. So many researchers are working on the halide double perovskites for some applications because these materials show promising solar cell absorber [21,69], tandom solar cell [69,70], photocatalytic [21,29,71,72] and light emission devices [21].

6. Challenges in Lead and Tin Free All-Inorganic Halide Double Perovskite Solar Cell

Unlike their encouraging efficiency, lead and tin based perovskite solar cells faced from both the toxicity of Pb metal and device instability [73–75], which limit the practical applications. Consequently, a great deal has been dedicated to the look for alternative perovskite materials such as lead and tin free halide double perovskites and lead and tin free all inorganic perovskites [76–81]. The great opportunity to use double halide perovskites is because of the following important points: 1) More stable to moisture compared to $(MA)PbI_3$. A 30-day exposure to 55% humidity [69] causes no decomposition in the material, whereas $(MA)PbI_3$ is mostly converted to PbI_2 [21,82].[6,82] Additionally, 2) halide double perovskites are more stable to heat compared to $(MA)PbX_3$. Volatile organics in $(MA)PbX_3$ perovskites leave the material at low temperatures. Although $CsPbI_3$ is more thermally stable, it does not form a 3D perovskite under ambient conditions. In contrast, the Bi-containing perovskites can be heated to ca. 350°C without decomposition [24,59,83]. Furthermore, 3) long photoluminescence lifetimes (660ns) [84], which are very promising for solar-cell applications and bandgap is ideal for pairing with Si absorbers in a dual-absorber tandem solar cell [83]. On the other hand, halide double perovskites have challenges relating to their physical chemistry and chemical physics, to date, which need further investigations for more advancement. Moreover, the lead halide perovskite solar cells have shown promise for low cost solar energy conversion (e.g., they have strong light absorption [85], long excited state lifetimes [85], efficient separation and transport of opposite charge carriers [86,87]. As a result, revolutionary advances have been claimed in lead halide perovskite photovoltaics, i.e., PCE has reached greater than 24.2% [31] for single junction organic inorganic halide perovskite in only a few years of development [88–90] and 25.2% for textured monolithic perovskite/silicon tandem solar cell [32], rendering lead halide perovskites as a unique type material for solar energy capture, but the record for Lead free all inorganic halide perovskite is 7.11%, and for both Lead and Tin free all inorganic halide double perovskite solar cell, the record is 2.50% [34] and 3.3% [43], which is far less than 24.2% for single junction and 25.2% for tandem solar cell, respectively. This creates big question and concern that can halide double perovskites solar cells really be an acceptable alternatives to replace organic inorganic halide perovskite solar cells in the market in order to realize the practical applications? [91]

The key challenging mechanisms during performance improvements are suggested as follows, which will be considered as core ideas for advancement:

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6.1. Discouraging Power Conversion Efficiency.

Regardless of the quick development of halide double perovskite solar cells, the cell power conversion efficiency remains about 2.5% which was achieved using $Cs_2AgBiBr_6$ [34] and 3.3% using Cs_2TiBr_6 [43]. Furthermore, the strategy to improve both material and device efficiency made of these materials becomes great concern. More interestingly, looking halide double perovskite light absorbers of high-quality with high absorption coefficient, longer diffusion length, free of defects, trap states with less radiative centers are assignment of this concern. In accordance with the Shockley-Queisser limit, a theoretical maximum PCE of 16.4% can be obtained with an Eg of 2.2 eV, thus holding promise for working double perovskite based photvoltaics [92]. Even though, the theoretical maximum PCE of $Cs_2AgBiBr_6$ does not reach the highest reported PCEs of single junction $MAPbI_3$ based photovoltaics, $Cs_2AgBiBr_6$ is a promising candidate for applications in tandem solar cells as it was already shown for $MAPbBr_3$, which features a slightly larger Eg of 2.3 eV [93]. Not only the energy alignment and band gap with the charge extraction layers, but also charge collection efficiency is vital to manufacture high-efficiency solar cells [60].

6.2. Mismatch among Various Interfacial Layers of the Device Architecture

This is another key challenge in halide double perovskite solar cells which remains unexplored area of research. Furthermore, poor interfacial integration might lead to broadening of the depletion width, poor band alignment, inefficient charge collection, enhanced recombination, insufficient charge transport and finally poor overall device performance. For instance, such mismatch in energy levels was occurred in materials such as $(MA)_2AgBiI_6$ and Cs_2PdBr_6. For example, $(MA)_2AgBiI_6$ was observed not compatible with TiO_2 but well-matched with SnO_2 and C_{60} [94].

6.3. Unclear Charge-Transport Properties of These Materials

Whether or not they're as favorable as for lead-based perovskites now is not well known. Lately, the optoelectronic properties of $Cs_2AgBiBr_6$ and combined antimony−bismuth halide double perovskites with the general system $Cs_2AgBi_{1-x}SbxBr_6$, which display comparable rate-transport mechanism to lead-based totally perovskites [16].

6.4. Quantum Confinement Effect

The quantum confinement effect in the last shells due to restricted orbital interactions of the adjacent cations particularly B′ and B″cations in the cubic unit cell of the $AB'B''X_6$ double halide perovskite materials might result a narrow and localized conduction band edge as well as broad energy gap, which deteriorate the device performance [29,91]. Consequently, finding way to move into another unite cell structure is expected to overcome such challenges.

6.5. Low Electronic Dimensionality

High dimensionality i.e 3D dimension of lead halide perovskites achieved high performance. The majority of these materials demonstrated 3D dimensionality [24], on the other hand, halide double perovskites showed broad bandgaps, which means structural dimensionality is a factor affecting PCE in addition to the electronic bandgap that is affected by the electronic dimensionality. This might make halide double perovskites inappropriate for single junction solar cell function though these materials crystallize into 3D [76].

6.6. Indirect and Wide Bandgap

Higher performance of organic inorganic halide perovskites was achieved due to their direct and lower bandgap, but halide double perovskites possess indirect and wide bandgap which limit absorption of light for solar cell and is not ideal for thin film PV applications cases and this field need bandgap engineering. For instance, in recent times bismuth and silver based perovskites were anticipated as a choice to replace $MAPbI_3$ [57,83]. The bandgaps are indirect, which is not ideal for

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single junction solar cell applications, though bismuth/silver based double perovskites absorb from 1.9 to 2.2 eV [95]. The reason that the indirect semiconductors are not preferable compared to the direct semiconductors is due to the weak oscillator strengths for radiative recombination and for optical absorption, which might be a challenge if there is low carrier mobility.

6.7. Energetic Disorder

Understanding energetic disorder in halide double perovskites becomes necessary of the time scales connected with atomic and molecular motion as well as the variation of the disorder from single crystal to the thin film. Knowing the variations might also be vital during processing of these light absorbing materials

6.8. Geometrical Constraints

There are variations reflecting the coordination and local chemistry. As these uncertainties transfer to the octahedral and tolerance factors, the stability ranges proposed so far are descriptive rather than predictive. There are some geometric factors restricting the formation of sTable 3D halide double perovskites. A lot of promising routes towards Pb-free halide double perovskites have been explored to replace Pb by elements such as germanium [56], bismuth or antimony and noble metals [57] [12,18,19,58–61] However, the geometrical constraints imposed by the necessity of forming an ideal perovskite lattice, in addition to the common oxidation states of these optional cations (e.g., +3 of Bi and Sb), still cause to be not easy the discovery of lead-free materials that could rival the optoelectronic properties of prototypes such as $MAPbI_3$.

6.9. High Processing Temperature:

While organic inorganic halide perovskites need annealing temperatures usually less than 100 °C, the halide double perovskites are only fabricated at higher annealing temperature up to 285 °C [40,96]. Such prerequisites for fabrication might damage the integration of the device architecture and further restrict wide range function of these materials. Additionally, such high energy consumption for materials fabrication is not economically cost effective, environmentally none green and is not sustainable. As a result, looking alternative methods that could minimize such higher processing temperature becomes an impressive research area in this field.

6.10. Shortage of a Broad-Spectrum of Speculative Guidelines

In spite of considerable contributions, there is no well refined guideline and theoretical understanding on what kind of mixed B-site cation halide double perovskites as well as on how to design Pb and Sn free halide double perovskites for enhancing collective optical, electrical, thermal and mechanical properties and long term stabilities of these materials for wide range applications. In order to minimize such bottleneck challenges, detail knowledge of the electronic structures of these materials with respect to of B′/B′′ cation arrangement and design become attractive research directions in the field of halide double perovskites.

6.11. Lack of Stoichiometric Design and Compatibility of Various Layers

Stoichiometric design of the perovskite [96] has been known as a strategy to develop solar cells with enhanced performance. Moreover, unique stoichiometric design and compatibility of various interfacial device layers are essential aspects that require more attentions in this field [20,28,97].

6.12. Incomplete Order

Elucidating the arrangement and position of the ions is another concern in halide double perovskites. Because the B cations generally determine the physical properties of double perovskites, there are three B-cation sublattice types known for double perovskites: random, rock salt, and layered. The latter two are ordered arrangements. In some situations it is observed that the order is

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not complete, especially in A′A′′B′B′′ X_6 structure. Interestingly, order-disorder effects are mainly come across when the charge variation between B′ and B″ is two or less. Although the degree of order is an important subject, the dynamic nature of order-disorder behavior is quite useful parameter [12,98–100].

6.13. Challenges in Achieving High Quality Films

Unlike organic inorganic halide perovskites, achieving high quality film in halide double perovskites become a challenge. High quality film might be defined as a material with excellent crystallinity, uniform morphology, less defects, high absorption coefficient, superior ambipolar carrier transport ability [101] and high coverage or pinhole free film [102,103]. All these parameters are well known to deter both materials and deviceperformance in halide double perovskite solar cells if the quality of these materials is not well optimized during processing steps. For that reason, the light harvesting and active layer that is the halide double perovskite monolayer in the perovskite solar cells is one of the very important research topic that researchers deal with. Moreover, controlling and designing the colloidal properties of the precursor and solvent engineering [104–106] should get a considerable attention to enhance the required film with high quality [107–109].

7. Suggested Research Roadmap Engineering Strategies for Material and Device Performance Improvement

In order to overcome the key challenging mechanisms faced by halide double perovskite solar cell, suggesting key areas of research, which will be considered as research roadmap for improvement of both material and device performance, is quite important. These includes engineering microstructure, surface and bulk properties, grain boundary and domain wall engineering, polar order engineering, bandgap and band structure engineering, colloidal engineering, composition engineering, optoelectronic engineering, device architectural engineering, interface and defect engineering, equilibrium and non-equilibrium quantum transport and ferroelectric engineering as shown in Figure 1.

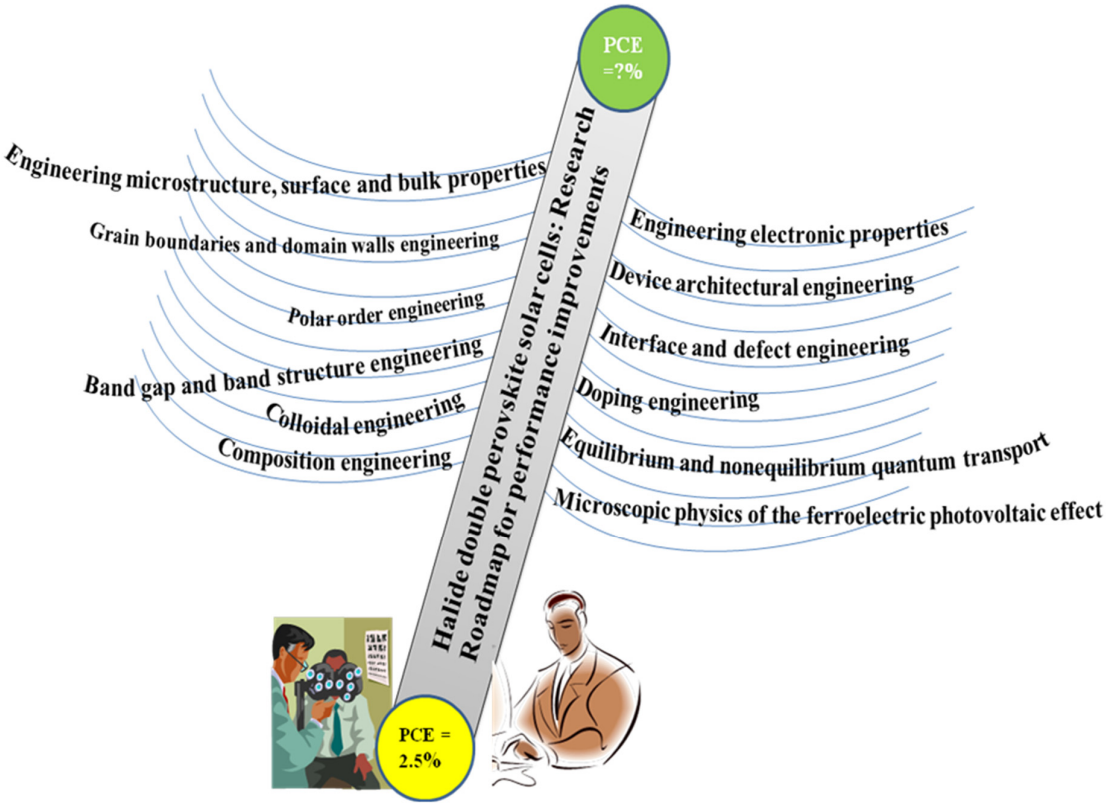

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Figure 1. Suggested research roadmap for performance improvement in lead and tin free halide double perovskite solar cells.

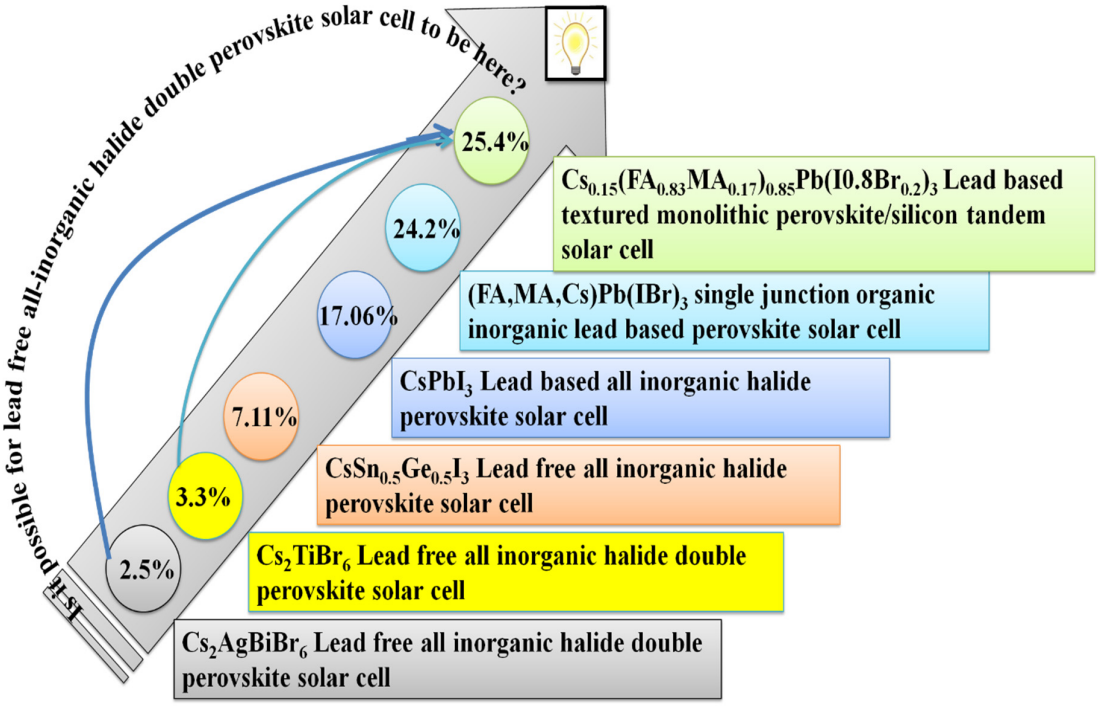

Figure 2. Comparison of power conversion efficiency of lead and tin free all-inorganic halide double perovskite, all-inorganic halide perovskite and lead based perovskite solar cell.

7.1. Engineering Materials Microstructure, Surface and Bulk Properties

Engineering microstructure, surface and bulk properties of halide double perovskites are important mechanisms and research areas for improvement for both material and device [110–114]. Microstructure influences virtually all aspects of the behavior of materials. Moreover, it is the spatial distribution of material in the useful object that is the goal of the endeavor and is the most richly variable, and thus the most susceptible to control, of the elements in the materials structural hierarchy. Engineering microstructure of materials [112,115] comprises the concepts of morphology or topological properties and geometry, thermodynamic properties, surface and bulk properties and grain growth as well as bulk and nanoscale domain structures.

7.2. Engineering Domain Wall and Grain Boundaries

The halide double perovskite microstructure might offer optional lanes for conductivity and electron−hole disjointing. Because grain boundaries have an impact on the long-term stability along with the ferroelastic domain boundaries that might be different from regular grain boundaries, the finding of ferroelasticity offers a novel parameter to regard as in the pursuit in favor of enhancing their stability as well as facilitating their extensive implementation [116]. Additionally, grain engineering and morphology control through the introduction of additives to the perovskite precursor is another way for performance improvement [32]. Sub-micron sized crystal grains in perovskite thin films, on the other hand, have been obtaining considerable attention due to their fundamental morphological properties in the course of twin domain [117,118], which are highly essential for understanding the basic mechanisms, for instance, low recombination rate and long diffusion length of the device's high performance [119]. Moreover, the presence of charged domain walls will significantly reduce the band gap by 20−40% and can serve as segregated channels for the

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motions of charge carriers, while the presence of uncharged domain walls has no substantial impact on the band gap [120].

7.3. Polar Order Engineering

Effect of polarization, molecular dipoles, tilting of octahedron and transition metal cation size and its oxidation states on photo-excitation, band structure, photoluminescence are not well investigated. Notwithstanding the microscopic model, polar order is accepted to recline at the center of the ferroelectric photovoltaic impact [121]. Besides, it is outstanding that interactions between lattice, orbital, and polarization order parameters in ferroelectric materials initiate upgrade of their physical properties close to phase boundaries [122]. On the road to advance performance, conventional approaches spotlight primarily on reducing the bandgap to superior fit the solar spectrum, departuring the basic relation between polar order and photovoltaic effect basically ignored [122].Hence spotlighting on both narrowing the bandgap and basic relation between polar order and photovoltaic effect become an attractive research topic this time.

7.4. Band Gap and Band Structure Engineering

The fundamental bottleneck restraining the function of halide double perovskites is their bigger energy gap [18,123–127]. The most favorable band gap for the single junction solar cells ought to be close to 1.3 eV [128]. As a result, band gap and bund structure engineering is vital if halide double perovskites are to be suggested optional contender materials [12,17,98,114,129,130].

7.5. Crystalization Process and Colloidal Engineering

The nucleation and growth, coordination chemistry and coordination engineering of halide double perovskites need to be studied: In addition to the photophysics properties, the nucleation and growth, coordination chemistry and coordination engineering concepts are equally important and quite essential for developing new halide double perovskite materials [131]. Therefore, colloidal engineering, colloidal chemistry and ion exchange reactions during synthesis of halide double perovskites are important ideas that need to be controlled for synthesizing high quality thin film for high performance.

7.6. Composition Engineering

Cation and anion displacement, cation-anion order disorder effects, cation size mismatch, distortion, tilting, ordered vacancies, hydrogen bonding, charge disproportionation and stereochemistry or lone air effects need to get more attention in order to improve stability, inferior material and device performance and engineering a new halide double perovskite materials [13,137,156–158]. In addition, creation of new chemical composition by using new elements in to the mixed halide double perovskite structure is an acceptable strategy to tune the band gap and of other optoelectronic peroperties [132]. Currently, $Cs_2AgBiBr_6$ and Cs_2TiBr_6 based lead and tin free all-inorganic halide double perovskites are reported as alternative type of perovskite solar cells. The later has energy gap of 1.8 eV in addition to its >100 nm carrier diffusion length [43]. The composition engineering due to modifications at the halide anion from Br to I results reduction in bandgap ranging from 1.0 to 1.8 eV [38]. This bandgap is suitable for single junction halide double perovskite solar cells [38]. Furthermore, modifications at the cation site, A-site and B site are not yet confirmed. Similarly, $Cs_2AgBiBr_6$ has high band gap which ranged from 1.83 to 2.21 eV [60,83,133]. Composition engineering at the A, B and X sites may reduce the bandgap to make it more suitable for single junction halide double perovskite solar cells [134].

7.7. Engineering Electronic Properties

Ferroelectrics, dielectrics, piezoelectrics, pyroelectrics, electro- and photocatalytic properties, thermoelectric properties, electrical transport properties and other optoelelctric properties are not yet studied [12,21,116,135].

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7.8. Interface and Defect Engineering

In the field of halide double perovskites, the interfacial properties especially between the active perovskite layer and the hole transporting layers is not well touched. Furthermore, the grain boundary interfaces present in the active perovskite layer in addition to the other grain boundary interfaces present between various layers is vital research lesson for improving the PEC and generally the performance. This is because considerable detrimental trap states in the electronic state of the valence and conduction band states of the halide double perovskite semiconductors might exist, which in turn increases the carrier recombination rate and reduces the open circuit voltage significantly [136–142]. Therefore, the engineering of the grain boundaries to eliminate the detrimental trap states in polycrystalline thin films becomes a long-standing and important issue for high performance optoelectronic devices [143–147]. In addition to the detrimental trap states, understanding the defect properties of the surface and bulk perovskite films, grain boundary and surface passivation mechanisms, defect properties of the interface during engineering the device architecture is quite crucial aspect, which need serious interface and defect engineering [143,144].

7.9. Device Architectural Engineering

Engineering the light harvesting active halide double perovskite layer and interface between the active layer and different charge transporting layers as well as between the transporting layers and the charge collecting electrodes are indispensable prerequisites for appreciable performance. However, engineering the materials and the interface among various layers are not adequate. This is due to the fact that the closing stages are eventually paying attention to the device performance for a specified appliance. As a result, engineering appropriate device architecture [148–150] is mandatory at the end of the day.

7.10. Doping Engineering:

This time halide double perovskites become less suitable solutions to replace the unstable organic inorganic halide perovskite solar cells. This is due to their indirect or direct as well as larger band gap [151–153]. Therefore, doping engineering [19,135,154–159], is another strategy to achieve a bandgap, which is suitable for light harvesting applications. This with chemical substitution approach might be done in all lattice sites of the double perovskite ($A_2(B^+,B^{3+})X_6$) available for substitution [160–162]. In this case, the degrees of freedom, with over 34 choices of trivalent metals available for selection is mostly provided from B^{3+} lattice site [163–165].

7.11. Equilibrium and Nonequilibrium Quantum Transport

These transport properties and effect of the spin-orbite on these properties are still unclear: Studies on these properties could shed light to provide insightful understanding on why inferior materials and device performance of halide double perovskites solar cells are happening.

7.12. Microscopic Physics of the Ferroelectric Photovoltaic Effect

This property becomes inadequately known as well as tarnished. Moreover, diverse methods have been suggested to explain research output in a variety of device architectures, such as, asymmetric momentum distribution of the nonequilibrium carriers [166,167], shift current through coherent evolution [168–170], polarization-dependent interfacial band bending [171,172] and bulk depolarization field [171].

8. Promising Candidate Properties to Substitute Pb Metal

The organic-inorganic halide perovskites become capable of photovoltaics and energy applications beyond photovoltaics. However, the large scale commercialization of the perovskite harvester faced considerable limitations due to the toxicity of lead metal in addition to the perovskite absorber degradation [6,74,99,173]. For this reason, there is an interest to discover nontoxic and stable

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perovskites for betterment of this field. The degradation concern can be treated by carbon encapsulation, multication substitution on top of incorporation of hydrophobic moieties [74,174], On the other hand, substitution of Pb using non-toxic transition metal atoms is the single strategy to overcome the toxicity problems [57,99,114]. Consequently, the optoelectronic properties [20,126,175–182] such as direct band gaps, defect tolerance, high absorption coefficient, small carrier effective masses, intrinsic thermodynamic stability, long charge carrier diffusion lengths, low excitons binding energies, higher dielectric constant and compatibility with low-cost and solution-supported fabrication procedures are considered as promising candidate properties to replace lead-based solar cell light harvesting materials in perovskite solar cells. Solving the predictable restrictions of solution-processed semiconductors are another important candidate topics that need to be considered in doing the lead replacement process [183–188].

9. Concluding Remark

Recently, lead free halide double perovskite solar cells have been reported as promising nontoxic and stable candidates to replace organic inorganic halide perovskite solar cells. Thus, such lead free halide double perovskite have (1) diversity of various families, (2) diversity of structural,optical and electrical properties and (3) wide range energy applications. Furthermore, the key origins of these diversities and variations are: cation displacement, cation anion ordering, ordered vacancies, tuneability of structural dimension, octahedral distortions and tilting from the ideal structure. In addition, polarization, molecular dipoles and tilting on the band structure are key orgins of optoelectronic properties in halide double perovskites. Although lead free halide double perovskite solar cells have promising opportunities such as relatively longer photoluminescence lifetime and higher stability towards moisture, temperature and light compared to lead halide perovskites, these solar cell devices still have bottleneck challenges both at material, interface and device level. Such challenges include a) inferior material and device power conversion efficiency, which is 2.5% Using $Cs_2AgBiBr_6$ and 3.3% using Cs_2TiBr_6, b) limited integration with interfacial materials, c) quantum confinement effect of interacting orbitals of adjacent cations, which might result broader band gap and localized conduction bands d) high processing temperature which may limit on the diverse applications, e) low electronic dimensionality making them less appropriate for single junction solar cell function. Thus, it is suggested that materials surface and bulk engineering, device architectural engineering, interfacial engineering, composition engineering, bandgap engineering, doping engineering, polar and domain order engineering, etc may be possible mechanisms to overcome the challenges. In addition, promising candidate characterstics, for instance, long charge carrier diffusion lengths, defect tolerance, low excitons binding energies, small carrier effective masses, intrinsic thermodynamic stability, direct band gaps, high absorption coefficient and compatibility with low-cost and solution-supported fabrication procedures are highlighted for further considerations. This review will serve as research roadmap for performance improvement of lead and tin free halide double perovskite solar cell scientific community, research institutions and commercial enterprises.

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