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# Perovskite Solar Cells: The Challenging Issues for Stable Power Conversion Efficiency

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Additional information is available at the end of the chapter

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## Abstract

Despite the advanced processing advantages for low cost, flexible and highly efficient solar cells, the technology is still facing the challenges with regard to the stability of materials in terms of moisture, thermal, light and oxygen atmosphere. The recent discovery of lead halide perovskite has increased a surge of interest in the field of photovoltaics. The chapter highlights some ways that can improve the stability and reducing the toxicity without compromising the efficiency of perovskite. Most of the part includes the review on the actual knowledge and cutting edge research results of high efficiency perovskites. It further describes the materials (Oxides and hybrid halides) that can be used for real time solar cell applications.

**Keywords:** halide-perovskite, photovoltaics, solar cells

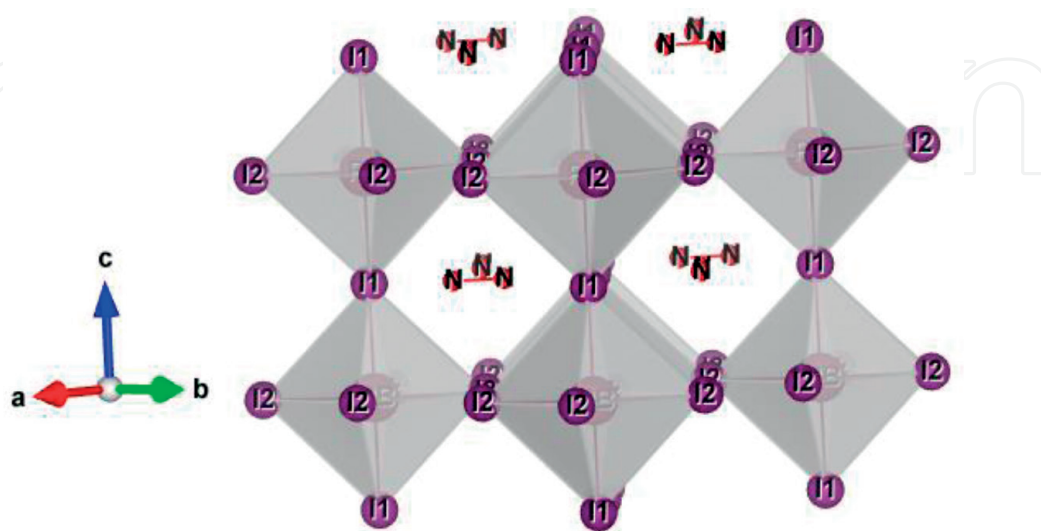
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## 1. Introduction

The rapidly growing rate of consumption of natural resources increases the demand for clean and everlasting option capable of providing indefinite and sustainable energy. Tackling with this global energy crisis is undoubtedly one of the most substantial scientific challenges of present era. Not only this, but the levels of greenhouse gases being emitted in the atmosphere are alarming, which reveals that the existing energy trends are also problematic in terms of economic and environment point of view [1]. Utilization of renewable sources and particularly solar energy provides the most solid alternative viable long term solution to this problem. The growing awareness about the urgency and benefits of solar energy systems will automatically push the efforts towards largely decarbonized energy systems. Arguably the most abundant and renewable energy source is sunlight with over 1000 W/m<sup>2</sup> of energy

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is falling at the surface of earth at sea level on clear sunny day. As a matter of fact, the solar energy that hits our planet in 1 hour is equal to the total amount of energy consumed by all humans of the world in a year. Indeed, coverage of less than 1% of the earth's surface would be sufficient to meet the world's energy needs using the latest commercially available solar panels. However, to compete the solar energy devices with fossil fuels in utility scale power generation, the necessary requirement is to reduce the total cost of solar energy either by low cost of solar device materials or by increased efficiency. Light energy conversion applications are of different types, among them photovoltaics consists of a number of established as well as emerging technologies. The solar cell is a photoelectric device which can directly convert solar energy into electric energy and offers the light absorbing capacity, long life cycle and less maintenance requirements. The first silicon based single crystal p-n junction solar cell was published in 1954 [2]. The study then increased exponentially over a half a century moving from crystalline silicon to inorganic, dye-sensitized, polymer and now perovskite solar cells. With regard to the commercialized modules, crystalline silicon devices are currently representing the 90% of global share [3]. Research and innovation over the years have led to the thriving performances of around 25% efficiency with a lifetime of 20 years in silicon based devices [4, 5]. This increased performance has forced many countries to initiate the economic programmes for producing electrical energy from renewable sources to civil and industrial sectors. During the last few years, the retail cost of silicon based photovoltaic devices/modules has reduced by ~70% which makes it possible to generate the revenues to develop this field further. Hence it makes some real image to realize innovative photovoltaic systems that can fulfill the actual demand of pollution free sustainable and stable energy. The perovskites is the most dominant of a wide family of materials with general formula  $ABX_3$  type in which A = organic cation, B = metallic cation and X = halide anion. The A cation is found to be somewhat larger than B. **Figure 1** represents the crystal structure of  $CH_3NH_3PbI_3$  perovskite a best known as a photoabsorbing material. Several properties such as ferroelectric, ferromagnetic, antiferromagnetic, piezoelectric, semiconducting, superconducting, conducting, insulating, catalysis etc. have been found in these materials since many years [6].



**Figure 1.** Typical perovskite crystal structure of  $CH_3NH_3PbI_3$ .

Organic solar cells have received an extensive amount of attention for renewable energy sources because of advantageous features such as low cost, flexibility, light weight and solution based fabrication [7]. However the first photovoltaic application was found in halide based perovskite  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_3, \text{Br}_3)$  by Miyasaka and his associates as an absorber material for the devices giving less than 1% power conversion efficiency for solid state cells [8]. The further optimization triggered in 2012 when the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (MAPI) and its mixed halide crossed the 10% efficiency mark [9, 10]. The progress has been observed rapidly over the years and the power conversion efficiency exceeds 20% using organo-lead halide perovskite [11, 12]. The most studied perovskites in terms of multifunctional applications are oxides due to their electrical, magnetic and ferroelectric properties. Halide perovskites initially received a little attention until layered organo-metallic halide perovskites were reported to exhibit a semiconductor to metal transition with increased dimensionality [13]. In 2013, perovskite solar cell technology was declared as one of the biggest scientific breakthroughs by the editors of Science and Nature [14]. However this breakthrough observed in solution based perovskites has drawback that the high efficiency can be obtained only in lead based perovskites which is arguably a substantial hurdle for various applications due to its toxic nature, even though the amount of concentration of lead is very less. This opens a new area of research to find some alternative approach for the replacement of lead without hampering the cell efficiency, durability and stability.

For future large scale solar photovoltaic, a material is required to meet some important parameters such as the material should be earth abundant, cost effective, and non-toxic. In addition, to achieve the high power conversion efficiency, the material must meet some principle properties such as electrical, optical and some defect properties such as direct tunable bandgap, absorption coefficient, and long carrier diffusion length. Many research groups took up the challenge to substitute the lead in order to find out some new non-toxic and stable perovskite materials suitable for photovoltaic applications.

Current efforts are under way to improve the stability and durability of perovskite solar cells. There are two main strategies which deserve an immediate attention to develop the stable solar cell and that is to protect the absorber from the external assaults by developing specialized functional barrier structures and to improve the resilience and stability of the absorber itself. These strategies are possible only by either altering the elemental composition of the perovskite or by modifying the perovskite absorber with functional molecules with the purpose of making them less susceptible to moisture degradation.

Lead free perovskite photovoltaics as light harvesting semiconductors have not yet benefited from the same intensive research effort that has propelled lead based perovskites from a power conversion efficiency of 3.8% to >20%. MAPI exhibits a number of remarkable properties that makes it an ideal contender for optoelectronic applications. The compound is a direct band-gap semiconductor with a room temperature band gap of 1.6 eV which is within the range of Shockley-Queisser gap for single junction cells [15]. Despite the processing advantages of perovskites, before the technology can be commercialized the poor stability of the organic-inorganic hybrid combinations with regard to the humidity, heat, light, and oxygen has to overcome. Recent reports have highlighted some innovative and elegant ideas which should be the main focus of future research for the design and practical applicability of photovoltaics materials [16]. Herein we highlight some recent advances in improving the chemical

stability of perovskite materials by substitution of cation and anion elements. Our hope is to pave the way for the design of perovskites to realize the stable and reliable perovskite solar cells with unprecedented improvement in stability.

## 2. Photovoltaic effect

The absorption of photons with energy above the bandgap ( $h\nu > E_g$ ) in a semiconducting material results the transfer of electrons from the valence band to the conduction band. In a particular material, the excited carriers will come back to the ground-state, with the energy being conserved by the emission of photons. The effect occurs when there is an asymmetric electric potential across the material and hence result the net flow of photogenerated charge carriers namely photocurrent. It is now possible to establish an asymmetric potential in a crystal such as p-n junction thereby giving a good rectification and hence better photovoltaic results. The good photovoltaic materials provide an opportunity to separate the charges as effectively as possible with minimal charge carrier relaxation by transporting them to the contacts and thus minimizing recombination between the electrons & holes. The overall power conversion efficiency represented by  $\eta$  of incident sunlight or power to electricity is directly proportional to the short circuit current ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ) and fill factor (FF). the overall equation can be written in mathematical form as:

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{in}}$$

The potential difference developed across the cell when the terminals are not connected is known as open circuit voltage  $V_{oc}$  which depends upon the bandgap of the absorber layer. The  $J_{sc}$  is the short circuit photocurrent extracted when the voltage across the device is zero which depends upon the range of spectrum absorbed by the active layer in a device. The expected power at the maximum power point observed in J-V curve as a function of power is known as fill-factor.

## 3. Desired properties for best solar absorber

There are several key properties that generally benefit device efficiencies. Many of these properties are very difficult to measure experimentally, however these can be obtained relatively very cheaply from theoretical perspective. Here we highlight some of the key features which needs to be addressed during device fabrication.

### a) Bandgap

The important property of a solar absorber is bandgap which determines the maximum theoretical power conversion efficiency. This is an intrinsic property and has eventually a direct influence on the actual performance of photovoltaic cell. The best solar cell efficiency can be achieved from the materials that possess band gap in the range of 1.1–1.56 eV. Bandgap is the property due to which we will be able to understand that whether the material is able to absorb the visible spectrum or not. How suitable the materials are for photovoltaic



applications would be determined by how close the photon energy is to the bandgap of the material. One of the promising strategies to realize the absorption enhancement is the synthesis of solar cell devices by using the materials having the bandgap as quantified by well-known Shockley-Queisser limit [17]. However to achieve the maximum efficiency, the bandgap of around 1.3 eV would be highly advantageous [18].

#### **b) Effective mass of charge carriers**

Some key features for photovoltaics solar energy generation is strong solar absorption, low non-radiative carrier recombination rates and the ability to capitalize for years. One of the important features is reasonably high carrier mobility for the development of solar cell architecture as it decides the range of properties accessible by forming mixed compounds within a compatible material. High charge carrier mobility plays an important role to establish the separation of electron-hole to improve the device performance. The dispersion of band edges particularly envisages the mobility in a material which is theoretically quantified by the effective mass of a carrier giving rise to smaller effective mass and thereby improves the carrier mobility. This carrier mobility is halted by scattering defects, phonons and other charge carriers. However, mobility is not the only important property, but the lifetime of minority carriers have also been considered to be an essential parameter for novel photovoltaic materials because of their role in Shockley-Read-Hall recombination mechanism [19]. Lot of parameters are necessarily required to achieve better performance among which high mobility, diffusion length, and long carrier lifetime are at the top as for as organic-inorganic halide composition is concerned [20].

#### **c) Optical absorption**

Optical absorption is among the important parameters and is playing a vital role to the development of high efficiency solar cells. Lot of studies have investigated that how the light-absorption of solar cells can be enhanced by forming antireflective surface techniques [21]. All photovoltaic devices exhibit a certain absorption threshold, and the energy of photons incident on the surface below the threshold do not contribute significantly to electricity conversion. It is noteworthy a strong absorption that can be achieved in a material having a direct bandgap, however, the materials with indirect bandgap may also perform well if a direct transition of suitable energy is also available. Strong absorption is characterized by sudden change in the absorption coefficient. The absorption coefficient reduces below the band edge without any deep states [22]. The absorption coefficient along with the optical band gap and high power conversion efficiency makes materials promising candidates for novel solar cell applications. The knowledge of absorption coefficient in a particular region where the absorber seems to be active is of paramount importance. Concrete information about the absorption coefficient of material provides the advantage over conventional materials and hence allows the fabrication of a desirable and thin cell structure.

#### **d) Ferroelectric and dielectric behavior**

Electric response is also playing a vital role to photovoltaic absorber. Considerable efforts have been made to optimize the properties of materials for photovoltaic use within the aim of converting sunlight very efficiently to electrical energy. The process requires the effective absorption of solar radiation to create the separation of photo-excited energy carriers and hence reduce the charge recombination rate as low as possible. Ferroelectric property provides

a viable route to separate charge carriers spontaneously and some noteworthy reports have also been published [23, 24]. However, most of the ferroelectric materials have wide bandgap ( $E_g > 2.8$  eV in case of  $\text{BiFeO}_3$  and  $E_g > 3.5$  eV for Lead-Zirconate-Titanate) that is beyond the visible light spectrum region allowing the use of just a mere percentage (10–20%) of solar energy. However, the ferroelectric behavior perhaps offers most obvious benefit with regard to a high degree of charge screening, and inhibits radiative electron–hole recombination. Having large dielectric constant in ferroelectric materials enables smaller defect binding energies promoting shallow defect states. Thus ferroelectric behavior has been of considerable interest with regard to the hysteresis.

#### e) Defect tolerance

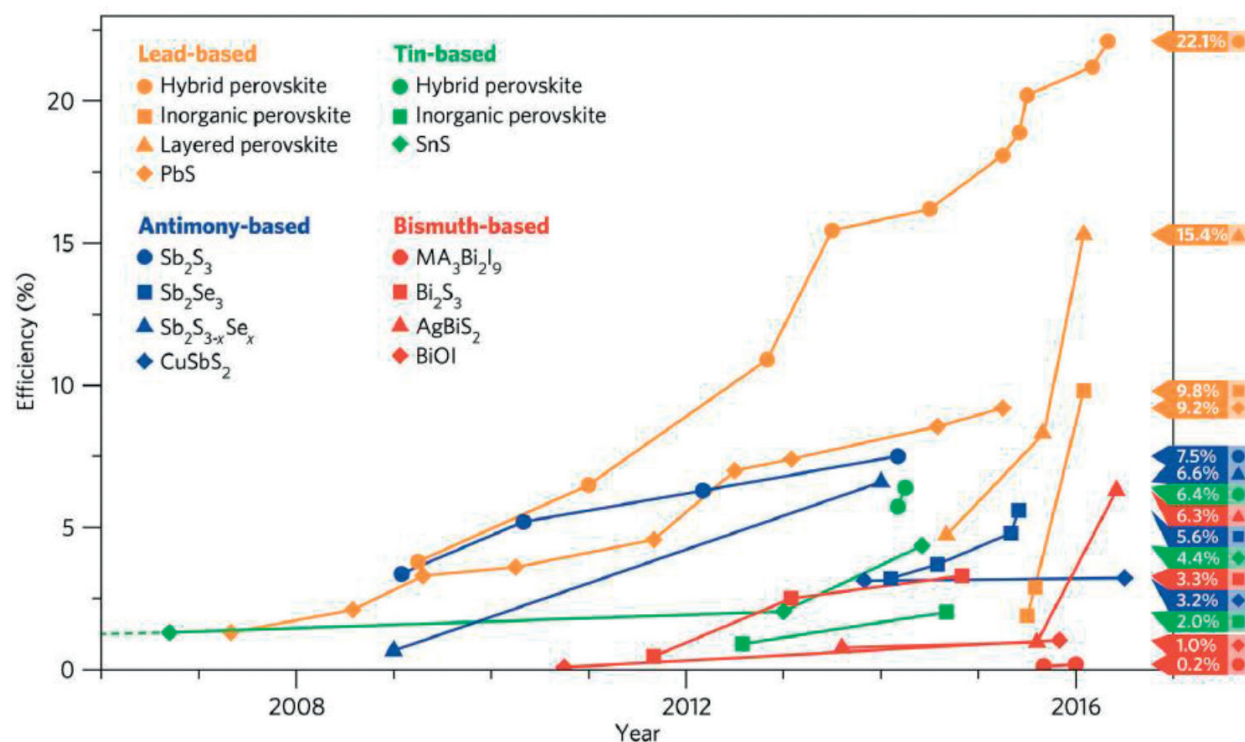
The physical properties of a material are generally dictated by impurities and defects. These imperfections exist fundamentally in two ways such as doping defects and impurities and create free carriers which enable charge recombination centers and charge scattering halts the mobility. Due to the strong interaction between the theory of defects and doping techniques, a lot of things have been understood about the physics and properties of defects. There are many routes that can be used to instill the defect tolerance in a compound and a specific approach can be adapted to design the device. From the application point of view an optimal material would combine the carrier concentrations with weak carrier scattering. The control on carrier concentration is the key factor in new generation quantum materials as the position of Fermi level which decides whether the specific band features are accessible. Recently, some compositions having  $ns^2$  lone pair such as  $\text{Bi}^{3+}$  and  $\text{Sn}^{2+}$  have been reported, considered to be an excellent contenders with defect tolerance features [25].

## 4. Replacement of lead in perovskite structure

Concerns however have been raised about the possible environmental and legal problems associated with new designs and technology of lead based solar cell fabrication. Lead, as a matter of fact is one of the most studied materials in terms of its toxicity and is found to be hazardous in environment which damages the nervous system and can cause brain disorder. Therefore, lead is unquestionably a problem and the serious efforts are required to phase out lead from the technological materials. Without degrading the favorable photovoltaic properties by replacing lead in perovskite structures by a non-toxic or comparatively non-hazardous compared to lead would therefore be a topic of interest. In this regard, the possibility of replacing lead by different element will be explored by taking the consideration of Goldschmidt rule and some additional quantum mechanical properties. It is very important to consider a very serious parameter while replacing the natural minerals and keeping the crystal structure more or less unchanged is a difference of electronegativity [26]. In addition the formability of halide perovskites depends on some key requirements such as charge neutrality between cations and anions, stability of  $\text{BX}_6$  octahedra and the ionic radii of A-site, B-site and the halide component. The octahedral stability can be understood by octahedral factor  $\mu$ , which is the ratio between the ionic radii of B-site and halide component while as the Goldschmidt tolerance factor predicted by ionic radii derives the stability range of perovskite. Keeping these things in mind one can provide a conceptual toolbox towards replacing lead

and some additional photo-physical properties of perovskite halides. Also this approach is exemplified by focusing on the ions having the ionic radii close to lead ion which should be non-toxic and relatively less expensive, of course without seriously degrading the overall performance of solar cells. Such replacement may be possible in the representative compound MAPbI<sub>3</sub> with comparable properties that suits the photovoltaics applications rather than single compound. Various efforts have been made to replace lead by using different ions having same or somehow near to the same ionic radii of lead which are mostly located in the immediate vicinity of lead in the periodic table. This suggests that they could be expected to have naturally a similar electronic structure. Many studies focused on the optimization of materials by testing alternatives at lead site and more than hundred unique combinations have been considered which form stable halide salts. **Figure 2** shows the combination of different solar photovoltaic absorbers used to improve the efficiency along with the stability. Thus an outstanding performance is based on the exceptional properties of halide perovskites exhibiting balanced electron-hole concentration, high absorption coefficient, direct and tunable band-gap, high charge carrier mobilities, and long carrier diffusion lengths etc.

Thus the current limitations impeding the commercialization of lead-based halide perovskite are now well known. These shortcomings are currently tackled by flood of research world-wide by using restless efforts from various research groups around the world to achieve good progress in the field. The stability issue was resolved by introducing the changes in the composition by mere loss of 5% of the initial power conversion efficiency [27]. However the toxicity issue is still an unsolved problem and many research groups took up the challenge to try the substitute of lead with other elements to solve the pending issues to make the materials stable, efficient and environmentally reliable. Therefore, some modifications



**Figure 2.** Improvement in the efficiency of different solar absorbers with years. [Source: Ref. 18].



of the well renowned MAPbI<sub>3</sub> compound must have the ability to increase the stability of the compound have become highly desirable. Depending upon the nature of the ions within the perovskite structure, a range of different divalent metal cations such as Pb<sup>2+</sup>, Ge<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Cu<sup>2+</sup>, Sr<sup>2+</sup>, Fe<sup>2+</sup>, Pd<sup>2+</sup>, Sn<sup>2+</sup>, Eu<sup>2+</sup>, and Mg<sup>2+</sup> have already been investigated at B-site of hybrid halide perovskites. By comparing the ionic radius for metallic cations with the oxidation state of +2 and after filtering with an ionic radius Pb<sup>2+</sup>, as in 6-coordinated systems according to Shannon, only nine elements are found to be feasible to substitute for Pb in perovskite structure. To avoid the mixed oxidation state, structural frustration and formation of vacancies in the structure, only three elements are perhaps found the perfect possibility to substitute for lead i.e. Ba<sup>2+</sup>, Ca<sup>2+</sup> and Sr<sup>2+</sup>. The corner sharing of BX<sub>6</sub> octahedra forms a three dimensional network in perovskite structure in which A-site cations occupy the 12-fold coordination to maintain the charge neutrality which is an important parameter for the stability of structure.

The most obvious choice for lead replacement is to see the group 14 metal, such as Sn or Ge and would be an important and fruitful development. Owing to their optical bandgap in the red or infrared region with outstanding carrier mobilities, these materials may constitute promising optoelectronic applications. Consequently the record efficiency for tin based halide perovskite lags behind that of lead halide perovskite. The low energy formation of tin based perovskite is because the oxidation state of tin transfers from +2 to +4 oxidation state upon exposure to ambient conditions, a transformation that does not occur easily in lead perovskites [28]. It was also noticed that tin perovskite had to be performed in nitrogen atmosphere to avoid the quick degradation of the samples. The tin based perovskites have also proved problematic making it difficult to achieve high device fill factor due to high rates of defect-mediated charge carrier recombination. Therefore, it is interesting to find other perovskite which may be more stable and reliable at ambient conditions for photovoltaic device fabrication. Beyond that, tin halide perovskites offer a variety of properties which make them attractive for use in photovoltaics provided the challenge with stability, including narrow bandgap, binding energies, and high charge mobilities than lead halides can be addressed.

The reports suggest that alkaline-earth metals such as magnesium, strontium, barium, calcium etc. can have the potential as substitutes to form perovskite structures due to their suitable ionic radii, abundance on the earth, +2 stable oxidation states similar to Pb<sup>2+</sup> except toxicity [29]. The simulations performed very recently reveals that Mg<sup>2+</sup> can replace lead in the structure by forming magnesium halide perovskites with optimum absorption, direct tunable bandgap within visible spectrum and low effective mass [30]. The bandgap has been found to be tunable by introducing different A-site cations. Despite the smaller ionic radius of Mg<sup>2+</sup> compared to lead, theoretical calculations predicted the stable halide perovskite structure [30]. Since magnesium based halide perovskite structures have not been explored as absorbing materials in solar photovoltaics yet, therefore, this composition requires some special attention.

It is well known that Ba<sup>2+</sup> has an ionic radius slightly larger than Pb<sup>2+</sup> and accordingly will also have a slight variation in the tolerance factor of compositions such as CH<sub>3</sub>NH<sub>3</sub>BaI<sub>3</sub> and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. However, the density functional theory (DFT) calculations have predicted that stable Ba based perovskite materials have bandgap of 3.3 eV which is quite large as compared

to Pb based compounds (1.57 eV). The reports suggest that the high bandgap is a reason of low electronegativity and low work function [29]. Also these halide perovskites have an issue of synthetic conditions due to their moisture sensitivity which hampers their synthesis formation, characterization and in particular their photovoltaic applications [30].

The best materials among the non-toxic, abundant and low cost alkaline-earth metal is none other than calcium ( $\text{Ca}^{2+}$ ) with an ionic radius almost similar to lead ( $\text{Pb}^{2+}$ ) and hence may be capable of filling the void as non-toxic element in halide perovskite structure [30]. However, as reported earlier, the high bandgap, instability in humid conditions, and less mobility hampers the calcium to be a suitable material for photovoltaics applications [31].

One of the obvious implementation has been done to find a lead free absorber in meso-structured perovskite solar cells such as  $\text{CsGeI}_3$  and  $\text{CH}_3\text{NH}_3\text{GeI}_3$ . However, the power conversion efficiency values were observed to be 0.11 and 0.20% respectively [32]. After some competitive efforts made to improve the efficiency in germanium based perovskites, a power conversion efficiency of approximately 3% in meso-structured cell architecture were claimed. The value is still much less compared to the theoretically possible PCE of >27% as predicted by Qian et al. [33]. Various efforts are still on the way to improve the efficiency of the said perovskites, however, for promising photovoltaic applications and full potential of the Ge based materials is by far not fully exploited yet.

Strontium is fairly a nontoxic and highly abundant metal on earth making it relatively an inexpensive with ionic radii almost similar to lead suggesting that exchange could be possible without affecting the crystal structure. Density functional theory revealed that strontium perovskite such  $\text{CH}_3\text{NH}_3\text{SrI}_3$  has similar bonding patterns leading to be a stable phase, despite the difference of electronegativity between lead and strontium [34]. The electronic properties of both Sr. and lead based halide perovskites revealed by simulation suggests that strontium has higher degree of ionic interaction as a consequence of lower electronegativity of strontium. This lower electronegativity together with the missing d-orbitals in the valence of  $\text{Sr}^{2+}$  is responsible for higher bandgap of around 3.6 eV. This is the main hurdle in Sr. based halide-perovskite that limits its possible application as an absorber material in photovoltaics technology. Another crucial issue related to  $\text{CH}_3\text{NH}_3\text{SrI}_3$  is the poor stability at ambient conditions due to its hygroscopic nature.

Transition metal halide and oxide perovskite structures were studied extensively over the decades particularly of their electronic and magnetic transport, magnetic properties, phase transitions and particularly of their high abundance [35–39]. As far as the transition metal oxides/halide perovskites are concerned with regard to their optoelectronic applications, various alternatives of lead-free transition metal perovskites have been predicted to be promising replacement candidates, however, the problems associated to their chemical stability, ionic radii hinders their functionality for photovoltaics. The factors responsible for the low photovoltaic performance from copper halide perovskites are low absorption coefficient, intrinsically low conductivity and high effective mass of holes. The small ionic radii of divalent iron metal ( $\text{Fe}^{2+}$ ) cation compared to lead effectively hinders the formation of three dimensional structures. Several compositions of iron halide perovskites have been studied with regard to their magnetic properties, very few research groups pay attention to the optical properties. The drawback that limits the stability of iron is its multiple oxidation states which follow the

same trend like germanium and tin based perovskites. Therefore a lot of survey is required by iron halide to find its applicability as an absorber for photovoltaic applications.

Rare-earth ions have been investigated in terms of optical applications such as  $\text{Eu}^{2+}$ ,  $\text{Yb}^{2+}$ ,  $\text{Tm}^{2+}$ , but the applicability of these materials in optoelectronic devices is limited due to their sensitivity towards moisture. Since the photovoltaic properties of lanthanides and actinides still have not been explored, however it is expected that these families may have some interesting optical properties and might be the potential absorbers for photovoltaic devices.

The most exciting developments have been initiated in the materials science of new halide perovskites with an emphasis on alternatives to lead. In the recent developments of new perovskites and perovskite-related materials was found that double perovskites have a potential to touch the new heights in the development of photovoltaic research [40]. Recently, various groups have started to work on double perovskite structures particularly on  $\text{Cs}_2\text{AgBiX}_6$  (CABX) family. The photoluminescence behavior of CABX has been studied by Slavney et al. and observed long decay time of the sample as reported in MAPbI<sub>3</sub> with an indirect bandgap of 1.95 eV which altogether is an attribute of long recombination lifetime [41]. The group also revealed stability of compound above room temperature after incorporated with bromide up to several days. A wide theoretical screening has been done using DFT calculations and observed that Ag compounds have higher bandgap while Au shares the lowest. The compounds such as  $\text{Cs}_2\text{AgSbI}_6$ ,  $\text{Cs}_2\text{BiAuBr}_6$  and  $\text{Cs}_2\text{BiCuI}_6$  are those observed to have bandgap within the optimal range [42]. It is clear that double perovskite structures allows us to replace the lead in the composition, however, their stability issue and high indirect bandgap may be a big issue to be resolved before their practical application in photovoltaic technology.

## 5. Modifications for better and possible photovoltaic materials

The instability with respect to the phase separation of MAPbI<sub>3</sub> due to the low formation energy has garnered significant attention to modify the compound in a way to increase the stability due to its record breaking efficiency. However, there are growing concerns surrounding its toxicity and long term stability. Here we will discuss about the other possibilities with the aim of identifying those combinations that will likely to achieve stable and high efficiency.

The method of turning the electronic properties of MAPbI<sub>3</sub> is by changing the organic cation. However, the formamidinium as a successful replacement for methylammonium has rather complicated the phase formation while its large bandgap adversely affects the device performance [43]. Instead of using organic cation, inorganic cation can be a best alternative to produce a compound an all-inorganic which may have some possibility to increase the stability. Various attempts made to replace A-site with other organic/inorganic cations have almost proved to be very challenging and difficult. Therefore, to introduce the inorganic cation at A-site by achieving a high efficiency will be a remarkable step towards the stability of perovskite photovoltaics. The tuning of stability and optical properties of a material can play a crucial role to enable the device moisture tolerant with exceptional absorbing characteristics.

The bandgap along with effective mass tuning is possible by replacing the ions in the structure. By replacing the organic part of perovskite structure may be more promising than inorganic one. It has been reported earlier that replacing the methyl ammonium content slightly with formamidinium ion in lead based perovskites can decrease the bandgap somehow and there are also some theoretical arguments which suggest that smaller cation could reduce the bandgap [44]. Therefore, the bandgap of strontium based perovskite may be reduced if the organic cation would be replaced by inorganic cation or changing the cation size will directly affect the geometrical changes such as tolerance factor and octahedral tilting. Since, inorganic counterpart such as Cesium is a best cation that can replace the organic part in the structure, but experimental evidence reveals that there is a problem related to the solubility of Cesium. Although a replacement of organic cation may decrease the bandgap which is the most crucial part to achieve the high performance of perovskites for solar cell applications. Thus the rise and emergence of hybrid perovskite (MAPI) has stimulated the photovoltaic research community. The only material till date is considered to be a third generation solar absorbing material that has a potential to effectively be an alternative to silicon technology. This material clearly possesses the property combinations that demonstrate the potential of polar materials for solar energy conversion.

## 6. Conclusion

The approach of utilizing Goldschmidt's rules together with additional quantum mechanical considerations can provide a promising route towards replacing lead, as well as providing general insights into the photovoltaics technology of metal halide-perovskites. The materials other than lead-halide perovskites appear to be more stable and exhibit some good functionalities, however the overall power conversion efficiency of these materials is low. Therefore it is very interesting to focus on the optoelectronic properties of the lead free materials in order to achieve the environmental friendly and stable photovoltaic perovskite devices. It is noteworthy that tin based solar absorbers and the group 14 metals have similar electronic properties, but still lead based devices outperform their tin based counterparts due to the oxidation of tin which leads to the efficiency loss. Several materials show some excellent solar absorbing property but they still require some development in their optical and environmental tolerant properties before they can reach to the comparable efficiencies. Therefore, it would be consequently from both toxicological, marketing and more importantly from legal perspective very beneficial if we succeed to replace the lead in perovskite solar cells without seriously degrading their overall performance. However, the lead free material combinations with robust optoelectronic properties with perfect stability at ambient conditions cannot be ruled out in near future.

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