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A review on recent progress in lead-free perovskite-based solar cell materials

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Chhabi Kumar Shrestha[1,2], Prakash Bhandari[3]*

1 Department of Physics, Prithvi Narayan Campus, Tribhuvan University, Pokhara, Nepal

2 Central Department of Physics, Tribhuvan University, Kirtipur, Kathmandu, Nepal

3 Kalika Secondary School, Rambazar, Pokhara, Nepal

Abstract: Although lead-based perovskite solar cells (PSCs) exhibit high power conversion efficiency (PCE), their global commercialization remains limited. It faces challenges due to the toxicity of lead, which raises environmental concerns. Consequently, researchers are focused on identifying such alternative elements that can replace lead without significantly changing its efficiency, stability, and cost-effectiveness. Therefore, this review focuses on potential candidates such as tin (Sn), bismuth (Bi), antimony (Sb), titanium (Ti), and copper (Cu), along with their properties, challenges, and possibilities. Furthermore, the double perovskites, which have emerged as a substitute route for obtaining stable, effective, and non-toxic PSCs, are also reviewed. Additionally, this review paper summarizes the methods for enhancing stability and efficiency by adding certain additives to create non-toxic and lead-free perovskites. Moreover, recent developments and advanced technologies employed in the development of lead-free PSCs are also discussed, along with their future direction.

Keywords: Perovskites • Photovoltaic cells • Optoelectronic properties • Efficiency

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I. Introduction

The population and hence energy demand are increasing daily. Most of the energy is derived from non-renewable sources, which are limited in supply and often considered dirty. Meanwhile, there are numerous options for renewable energy sources, including wind, solar, tides, and rain. Among them, the sun is the cheapest and cleanest renewable source of energy because it is inexhaustible and abundant [1].

The solar cells convert the incident photons into electrical energy through photovoltaic devices, which were first discovered by Edmond Becquerel in 1839 [2–4]. Solar cells are favourable due to their low maintenance requirements, affordable power supply, suitability for distant locations, sustainability, low carbon emissions, environmental friendliness, and renewable nature [5, 6]. Typically, the solar cells

* *Corresponding Author: prakashbhandarijob@gmail.com*

consist of the light-absorbing layer, which is the most important part of the solar cells, placed between the electron transport layer (ETL) and hole transport layer (HTL) as depicted in Fig. 1. When the solar cell is exposed to sunlight, then charge carriers (electrons and holes) are generated, and due to the movement of these charge carriers, an electric current is produced.

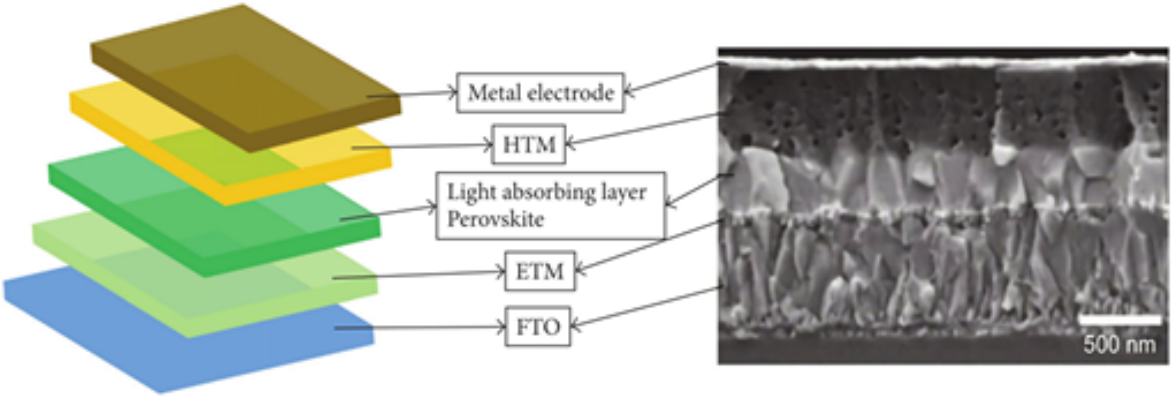

Figure 1. Perovskite solar cell structure [7].

Solar cells can be divided into four generations. The first generation includes wafer-based solar cells, the second generation includes thin-film-based solar cells, the third generation includes organic photovoltaics, and the fourth generation includes hybrid-type solar cells [8]. First, second, and third-generation solar cells have been in use for many years, but their use is limited by their high cost, complex preparation technology, and unfriendly character. Therefore, researchers are searching for environmentally friendly and reasonably priced solar cell materials. Some of the reported solar cells are single-crystalline and polycrystalline solar cells, CIGS solar cells, CdTe-based solar cells, quantum dot solar cells, organic photovoltaics, and perovskite solar cells (PSCs). Due to its exceptional photovoltaic potential, organic-inorganic lead halide PSCs have demonstrated power conversion efficiencies (PCEs) of over 26% in small-area single-junction cells and over 33% in perovskite-silicon tandem cells [9]. Perovskite structure refers to materials with the generic form ABX_3 and has the same crystalline structure as that of perovskite, where A = Cs^+, $CH_3NH_3^+$, $HC(NH_2)_2^+$, B = Pb^{2+} or Sn^{2+}, and X = I^-, Br^-, Cl^-. Fig. 2 shows the typical cubic perovskite crystal structure.

A perovskite light absorber layer is used in perovskite solar cells. This class of perovskite materials has high electron and hole mobility [10–13], good absorption properties [14–16], a good band gap [17, 18], low-temperature solution processability [19–21], long carrier diffusion length and lifetime [22–24], low exciton binding energy [25], low defect density [26, 27]. Despite its remarkable efficiency, some disadvantages hinder its global commercialization, i.e., stability problems and the toxicity of lead. When lead is used in solar cells, it can easily degrade and may cause environmental and health issues due to its

hazardous nature. In addition to the toxicity of lead, some countries have implemented regulations to ban the use of this toxic element in electronic equipment [28]. Furthermore, due to the presence of lead, it is very difficult to ensure the safe recycling and disposal of lead-based solar cells at the end, as improper handling can contribute to environmental contamination. Therefore, the development of lead-free perovskite is important not only in reducing toxicity but also to meet legal requirements and for long-term stability. In place of lead, we may use metal elements like tin (Sn), titanium (Ti), germanium (Ge), silver (Ag), bismuth (Bi), copper (Cu), etc. [29]. Again, to improve the stability, one can replace two Pb^{2+} cations with one tetravalent M(IV) cation to form the double perovskite $A_2M(IV)X_6$ or replace three Pb^{2+} by two trivalent M(III) cations to form $A_3M(III)X_9$. Similarly, to absorb the light by a sufficient amount, we can replace the B-cation with M(I) and M(III) to form the quaternary double perovskite. The performance of solar cells is measured in terms of power conversion efficiency (PCE), which indicates how effectively incident sunlight is converted into usable electricity. Achieving a high PCE for lead-free perovskite is crucial to ensure that the removal of toxic lead does not compromise solar cell performance. Developing lead-free materials that offer both high efficiency and good stability is vital to the practical implementation of environmentally friendly perovskite solar cells. In this review, we briefly discuss the recent development of lead-free PSCs and alternative possible elements that can be used in place of lead in PSCs [30].

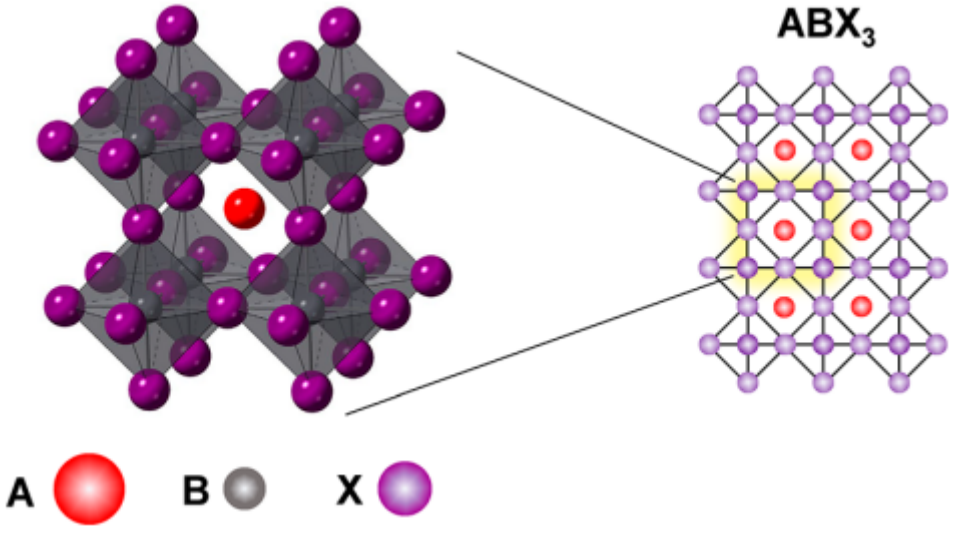

Figure 2. Three-dimensional perovskite crystal [31].

II. Methodology

In this review, we examined approximately seventy articles published in peer-reviewed journals between 2012 and 2025, collected from the Google Scholar database. The articles are selected using key-

words such as “toxicity-free”, “lead-free perovskite”, and “sustainable solar cells”. The literature addressing lead-free perovskite solar cells, environmental concerns, and solar cell design is included. Literature which are outside the scope of solar energy applications, non-peer-reviewed papers, conference papers, and lead-containing perovskites, is excluded. Based on stability, efficiency trends, and environmental effects, we have extracted the data. It provides a comprehensive examination of recent developments in lead-free perovskite solar cells, employing an analytical approach. It draws attention to those important areas that need further research and helps to advance the continuous development of efficient, stable, and environmentally sound perovskite-based solar cells.

III. Recent progress on lead-free perovskites

Tin-based perovskites

Tin is considered the prominent candidate that can be used in place of lead-based perovskite. Its electronic structure is the same as that of the lead but of a smaller ionic radius (1.35 Å) than that of Pb (1.49 Å) [32]. Tin is non-toxic and inexpensive, exhibiting similar electronic properties to those of lead. Due to its remarkable performance, like a narrow band gap, excellent charge mobility properties, and low exciton binding energy, it is considered the most promising alternative element to make lead-free PSCs. Although it offers some advantages, it also has some demerits, including high conductivity, which results in poor performance in photovoltaics and reproducibility [33]. It is due to the unstable divalent Sn state in the structure. Additionally, due to its high defect densities, rough morphology hinders the efficiency of solar cells.

In 2016, Chen et al. prepared $CsSnX_3$ (X=Cl, Br, and I) perovskite and obtained the power conversion efficiency (PCE) of 12.96% when it was illuminated by AM 1.5 G [34]. The compound $CsSnI_3$ shows a direct band gap of 1.3 eV at room temperature, and it is nearly 10 times more stable than methylammonium lead iodide perovskite. The reason behind the higher performance is due to the higher fill factor (FF), which is achieved by the co-deposition of perovskite precursors with $SnCl_2$ [35]. In 2012, Chung et al. experimentally observed that the perovskite $CsSnI_3$ exhibits high electrical conductivity, good photoluminescence, and effective light absorption [36]. So, Sn-based perovskite could be a good strategy to replace lead. Similarly, for $CsSnCl_3$, a PCE of 9.66% is achieved with a fill factor (FF) of 56%. For $CsSnBr_3$, a PCE of 10.46% and an FF of 58% have been achieved [34]. Also, $CsSnBr_3$ showed better thermal stability than $MASnBr_3$ [37]. Qui et al. used Cs_2SnI_6 PSCs for the light-absorbing layer and obtained a PCE of 1.0% [38]. Due to their poorer electronic properties than those of the Pb-based PSCs, they do not have good photovoltaic properties. Noel et al. [39] experimentally studied $CH_3NH_3SnI_3$ as the light-absorbing layer and obtained the PCE of 6.4%. Although the electronic configuration of tin is the same as that of lead and is non-toxic, its efficiency is low and unstable in the air. Using a simulation

technique through SCAPS-1D, Farhana Anwar et al. observed the efficiency of $CH_3NH_3SnI_3$ based PSCs of 20.23% [40]. In 2015, Koh et al. employed $FASnI_3$ as a light-absorbing layer for lead-free PSCs [41]. One of the major problems for Sn-based perovskite is the oxidation of Sn^{2+} to Sn^{4+} when it is exposed to air, which causes the formation of traps and degradation of the material [42].To address this problem, the addition of SnF_2 on the Sn-based perovskite is carried out, which reduces the background charge density by neutralizing traps through filling the cation vacancies [43]. The addition of SnF_2 to the $FASnI_3$ compound results in an efficiency of 2.10%. Additionally, encapsulation techniques can be employed to protect the Sn-based perovskite from moisture and oxygen, thereby increasing its stability.

Bismuth-based perovskite

Bismuth is a group 15 element, and the electronic configuration of Bi^{3+} is $6s^2$. Due to its exceptional photovoltaic performance, non-toxicity, environmentally friendly nature, and high stability under heat and moisture, it can be used as a replacement for lead in PSCs. The ionic radius of Bi (1.03 Å) is nearly comparable to that of lead (1.19 Å) [44]. It has a band gap in the range of 1.79 eV to 1.83 eV, and a PCE of 18% has been achieved [45]. Although Bi-based PSCs are non-toxic, lead-free, and stable, their practical applications are limited due to their poor surface morphology and relatively large bandgap energy. Here, we have reported some of the perovskites that have been studied. A two-step evaporation spin-coating process was used by Ran et al. in 2017 to create the $MA_3Bi_2I_9$ thin film that produces a homogeneous and pinhole-free surface having a PCE of 0.39% [46]]. In 2017, Turkevych et al. studied the optoelectronic properties of Ag_3BiI_6 perovskite and observed the PCE of 4.3% [45]. In methylammonium bismuth iodide (MBI); $(CH_3NH_3)_3Bi_2I_9$ single crystal, Kawai et al. detected an exciton band at 2.51 eV with a high binding energy of more than 300 meV [47]. MBI films are composed of nanoclusters encircled by insulating $CH_3NH_3^+$ ions. This results in significant interactions between the localized and delocalized exciton, which causes anisotropic photoluminescence [48]. A large number of Bi-based compounds are identified, which include $AgBi_2I_7$, $BiFeO_3$, $BiFe_2CrO_6$, $BiMnO_3$, and $Cs_3Bi_2I_9$, and their optoelectronic properties are studied. Although it is stable, non-toxic, and environmentally friendly, its efficiency is lower than that of the metal halide perovskite, which may be due to the large indirect band gap and poor film crystal quality.

Antimony-based perovskite

Antimony belongs to group 15 in the periodic table, which has an ionic radius of 0.76 Å and its electronic configuration is $5s^2$ [49]. It could be a safer and more affordable element that can replace Pb in solar cells. In 2018, Yu-Liang Liu et al. studied the optoelectronic properties of $Cs_3Sb_2X_9$ and observed that $Cs_3Sb_2I_9$ has a high value of electron mobility [50]. So, it is suitable for the generation of hydrogen and the reduction of CO_2. Due to the large difference in the electron and hole mobilities, the recombi-

nation of charge carriers decreases, and its photocatalytic efficiencies can be improved. So, $Cs_3Sb_2I_9$ is considered an alternative candidate to replace Pb-based perovskite solar cells. But Sb-based perovskites also possess drawbacks. They tend to produce a dimer phase with poor photovoltaic properties when they are synthesized via solution processing [51]. Dimer perovskite shows an interesting subset of metal halide clusters or isolated metal halide octahedral anions, while the layered structure is made up of 2D folded layers with partially corner-sharing octahedra. Overall, dimer perovskites exhibit strong exciton binding energy and excellent stability in ambient circumstances. Direct band gap, small optical band gap, and effective charge carrier transport characteristics are all present in the layered perovskite. In thermodynamic terms, the layered phase is less favorable than the dimer phase [52]. For instance, because of its amorphous nature, pinholes, and rough surface, methylammonium antimony iodide $(CH_3NH_3)_3Sb_2I_9$ produces a zero-dimensional dimer of low PCE [53]. Researchers are intensively studying techniques to overcome these shortcomings and optimize the performance of Sb-based perovskites. Here, we briefly discuss the Sb-based perovskites. $Cs_3Sb_2I_9$ is one of the Sb-based perovskites, which is more stable than methylammonium lead iodide perovskite film when exposed to a similar environment. It is noted that the divalent $Pb_2{}^+$ cation in $(CH_3NH_3{}^+)(Pb_2{}^+)I_3{}^-$ has a similar electronic configuration as trivalent $Sb_3{}^+$ in $(Cs^+)_3(Sb_3{}^+)_2(I^-)_9$. Therefore, Sb can be considered one of the promising alternative candidates to lead [54]. The perovskite $Cs_3Sb_2I_9$ exhibited a PCE of 1.5% [51]. There is another perovskite $(NH_4)_3Sb_2I_xBr_{9-x}$ $0 \leq x \leq 9$, which is nontoxic, low-cost, and environmentally friendly, and that dissolves well in ethanol, in which its composition allows us to tune the iodine and bromine content. For $(NH_4)_3Sb_2I_9$ perovskite, the PCE of 0.5% was reported [55]. The perovskite $(CH_3NH_3)_3Sb_2I_9$ was fabricated by Hebig et al. in 2016 and exhibited a PCE of 0.5% [56]. Similarly, Weber et al. explored the lead-free perovskite compound $Rb_3Sb_2I_9$ as an absorbing layer and exhibited PCE of 1.37% [57]. The highest recorded efficiency for Sb-based perovskite so far is 2.77% as determined by Karuppuswamya et al. [53]. This finding suggests that further research is needed to achieve higher efficiency in lead-free Sb-based PSCs.

Titanium-based perovskite

Titanium (IV) is a transition metal that belongs to Group 4 (IVB) of the periodic table. It has an ionic radius of 0.53 Å and an electronic configuration $4p^6$. It is an abundant substance that is nontoxic and more stable. However, properties such as undesirable defects and inappropriate band gaps are challenging for the widespread adoption of perovskite solar cells. Titanium could be a better alternative for perovskite solar cells. Titanium-based perovskite, like Cs_2TiBr_6, fabricated by Chen et al., achieved a band-gap of 1.8 eV with a PCE of 3.3% [58]. The report shows that further improvement is achieved by adding a C60 layer on Cs_2TiBr_6 high pressure (HP) thin film and TiO_2 as ETL. Ju et al. reported that Ti-based PSCs demonstrated high intrinsic and environmental stability [59]. The bandwidth of thin-film

mixed halides, such as $CS_2TiI_{6-x}Br_x$, increases with the Br content. This lowers the optical performance and absorption. Rb_2TiBr_6 is a ductile, stable direct band-gap semiconductor (1.59 eV) with strong visible light absorption. The hybrid Ti-based perovskite Cs_2TiI_6 shows promising optoelectronic properties. Ti-based PSCs achieve an efficiency of up to 3.28%. The highest efficiency of Ti-based perovskite is smaller than the efficiency of tin but is greater than that of antimony-based perovskites. In addition, the voltage that appears with Cs_2TiBr_6 perovskite is much higher compared to other Sn-based ones, and it is 1.02 V [60]. Although it has low efficiency, the absorption coefficient is higher and possesses a favorable band gap, making it a suitable perovskite solar cell alternative to the poisonous lead. Ahmed et al. experimentally observed a PCE of 8.66% for Cs_2TiBr_6 and an FF of 86.45% [61].

Copper-based perovskite

Copper belongs to group 11 (IB) in the periodic table, with its ionic radius of Cu^{+2} is 0.73 Å with $3d^9$ as the electronic configuration. It is naturally available and reactive, forming a compound that can be used as an alternative perovskite with a high absorption coefficient. It exhibits high stability and large charge mobility, and its strong light absorption capacity in the visible region has drawn attention to lead-free perovskite solar cells. Copper-based perovskites often exhibit 2D structures with quantum well-like electronic, magnetic, and dielectric properties [62]. However, a smaller ionic radius limits halide octahedron networks, causing low absorption and conductivity. The perovskite-like $(C_6H_5CH_2NH_3)CuBr_4$, fabricated by Li et al., has high stability to moisture, UV light, and temperature. It shows a low band gap of 1.81 eV and a high absorption coefficient of nearly 10^5 cm^{-1} and a carrier lifetime exceeding 2 ns, so it is suitable for a light harvester [63]. This band-gap can be maintained and improved by increasing the Br content. The double-layered, eco-friendly solar cells, using two copper-based perovskite-like compounds, $((CH_3(CH_2)_3NH_3)_2)-CuBr_4$ and $(p\text{-}F-C_6H_5C_2H_4-NH_3)_2-CuBr_4$, with PCEs of 0.63% and 0.51%, respectively, might be an alternative to toxic Pb-based and unstable Sn-based PSCs [64]. The study of Cortecchia et al. shows that $MA_2CuCl_xBr_{4-x}$ perovskites have tunable band gaps (1.80-2.48 eV based on Br/Cl ratio) and Cu^+-driven luminescence, but Cu-based PSCs still suffer from the highest efficiency of just 0.63%. Such a low PCE of copper perovskite is due to the heavy mass of holes and low absorption coefficient because of their smaller ionic radius. Several studies are underway to increase the efficiency of copper-based solar cells.

Double perovskite

Double perovskites $A_2BB^{'}O_6$ are derived from the general perovskite structure ABO_6. Double perovskite shows a quantum size effect and hence enhances the stability due to the added surface energy of the nanoscale phase. Materials like Cs_2AgBiI_6 are difficult to make in bulk but are stable. Double perovskites exhibit small as well as flexible and tunable band gaps and electronic properties due to their quaternary

nature. Lead-free variants, such as $CS_2SbAgCl_6$, exhibit excellent optoelectronic performance, stability, and eco-friendliness, making them ideal for use in LEDs, solar cells, and sensors. Their combinatorial compositions and low carrier masses enhance applications in renewable energy and optoelectronics. They show outstanding optoelectronic properties due to their suitable band gap spanning the visible region and low carrier effective mass. Some double perovskites like $Cs_2SbAgCl_6$, $Cs_2InAgCl_6$, and $Cs_2BiAgBr_6$ are suitable potential alternatives because their band gaps lie in the visible range [65]. Another double perovskite, Cs_2NaBiI_6, Zhang et al., reported in 2018, that it is cost-effective with a lower band gap of 1.66 eV with a broad absorption range. It also has greater stability against air and moisture with a lower PCE of just 0.42% [66]. $Cs_2AgBiBr_6$ can achieve 1.06 V of V_{oc}, and 5.13 mA cm^{-2} of Jsc with the highest PCE of 2.84% [29]. This efficiency can be increased by optimizing inputs more effectively. The combination of other metals may be a possible way to replace toxic lead-based PSCs, leading to higher efficiency. The PCE of the studied perovskites is summarized in Table 1.

Table 1. Power conversion efficiency of perovskite-based solar cells

S.N.	Materials	PCE (%)	References
1	$CsSnI_3$	12.96	[34]
2	$CsSnCl_3$	9.66	[34]
3	$CsSnBr_6$	10.46	[34]
4	Cs_2SnI_6	1.0	[38]
5	$CH_3NH_3SnI_3$	6.4	[39]
6	$CH_3NH_3SnI_3$	20.23	[40]
7	$FASnI_3$	2.10	[41]
8	$MA_3Bi_2I_9$	0.39	[46]
9	Ag_3BiI_6	4.3	[45]
10	$Cs_3Sb_2I_9$	1.5	[51]
11	$(NH_4)_3Sb_2I_9$	0.5	[55]
12	$(CH_3NH_3)_3Sb_2I_9$	0.5	[56]
13	$Rb_3Sb_2I_9$	1.37	[57]
14	$(CH_3NH_3)_3Sb_2I_9$	2.77	[53]
15	Cs_2TiBr_6	3.3	[58]
16	Cs_2TiBr_6	8.66	[61]
17	$(p\text{-}F\text{-}C_6H_5C_2H_4\text{-}NH_3)_2\text{-}CuBr_4$	0.51	[64]
18	$(CH_3(CH_2)_3NH_3)_2\text{-}CuBr_4$	6.63	[64]
19	Cs_2NaBiI_6	0.42	[66]
20	$Cs_2AgBiBr_6$	2.84	[29]

IV. Future Perspectives

Advanced research suggested that some elements, like Ge, Sn, Sb, Bi, etc., could be the most probable alternatives that can be used in place of lead because they have a similar outer electronic structure to that of lead. Now, the fabrication techniques and suitable additives, such as Butylammonium iodide (Bai), Ethylene diammonium diiodide ($EDAI_2$), SnI_2, SnF_2, and $SnCl_2$, can enhance the efficiency and stability of lead-free PCSs. Some investigations have proposed that metal-free organic perovskites and chalcogenides could be used in recent solar cells due to their outstanding optoelectronic features, which is

in favor of both experimental and theoretical studies. The modern challenge is to enhance the efficiency and stability of PCSs for long-term durability and optimal performance. To obtain higher efficiency, it is necessary to use an optimized quantity of such an additive that maintains the lower band gap or constant optical band gap and its width. These challenges can be improved by addressing material stability, understanding the functional mechanism, designing the charge transport layer logically, and applying the profound knowledge of photodynamics. On the other hand, numerous studies have been conducted to mitigate the toxicity caused by lead leakage. This problem can be mitigated by encapsulating lead with different functional layers and by proper management of PSCs. Chalcogenide and germanium-based perovskites have recently drawn interest as potential lead-free substitutes because of their appropriate band gaps and reduced toxicity. These materials exhibit promise for enhanced stability and optoelectronic performance, despite their early beginnings. Encapsulation of PSCs can be done by adding hydrophobic transparent insulators, a UV reflector having a suitable reflective index [67], and materials like resins UVR-C (front), C100(black) [68], sulphonic acid-based resin [69], alucone, and Al_2O_3 bi-layer stack, etc. [70].

V. Conclusions

In this review, we have discussed some promising alternatives to lead-based perovskites, highlighting their efficiencies as potential better practical alternatives. Based on the studied compound, Sn-based perovskitlike $CH_3NH_3SnI_3$ exhibits a PCE of 20.23%, which is the highest, making it a promising alternative. The method of improving stability, efficiency, and reducing the toxicity of lead has also been discussed. Furthermore, this review has explored the current developments and future possible technologies that enhance the efficiency of solar cells. Finally, continuous research and innovation in device engineering and material design are crucial to realizing the potential of non-toxic and sustainable photovoltaic technologies.

VI. Acknowledgment

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