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Lead-free Perovskite Materials for Solar Cell: An Update of Recent Trends

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Abstract: Solar energy has emerged as renewable energy to support human and social development. The development of low-cost, high-efficiency perovskite solar cell has attracted intensive attention because of unique properties such as band gap tenability, stability and high absorption co-efficient value. Research indicates that the power conversion efficiency of lead perovskite solar cell has increased from 3.8% to 25.2% recently. However, the main challenges in this type of solar cell was lead element. Lead is very toxic and very hard to discharge from the body. Therefore, researchers work hard to develop non or low toxic metal ions to substitute lead in solar cell. In this work, different lead-free perovskite materials (tin, germanium, caesium, copper, bismuth and antimony) and related photovoltaic behaviors were reported. The band gap, absorption efficiency, power conversion efficiency, fill factor, short circuit current, open circuit voltage and other physical properties for all of lead-free materials were highlighted. Tin based perovskites showed very high absorption coefficient. Bismuth and antimony were very stable because of +3 valence state in the atmosphere. Finally, the review also describes some challenges facing the performance of solar cells.

Keywords: Absorption, band gap, Lead-free, perovskite materials, power conversion efficiency, semiconductor, solar cell.

1 Introduction

The increasing energy demands along with rising climate concerns has necessitated the energy generation from sustainable, affordable and environmental friendly resources. Photovoltaic (PV) technology has got a promising potential to fulfill the world's growing energy demands in an eco-friendly way as the crystalline silicon (c-Si) based solar cells achieved efficiency of 26.7% [1], which is almost 2% below their thermodynamic efficiency limit [2]. However, the high fabrication costs of c-Si solar cells (heating c-Si ingot at 1000 ℃) have moved the researchers to explore emerging materials that can provide relatively higher power conversion efficiency at low production cost. Generally, formula ABX_3 could be used to represent perovskites. Anion and cation were indicated by "X" and "A, B", respectively [3]. No other solar cell technology has seen such dramatic emergence and unprecedentedly rapid development as perovskite solar cells (PSCs) with their efficiency has already approached 25% in a very short timescale [4].

Perovskite has some amazing photoelectrical properties such as the high power conversion efficiency (>25% [4]), cost-effective fabrication, low temperature processing [oxidative chemical vapor deposition] and high absorption coefficient [5] that have made it a promising candidate to replace the existing c-Si technology. The minority carrier lifetime ($\tau \sim 10\, ns$) and carrier mobility ($\mu \sim 40\, cm^2/V.s$) for perovskite are relatively high as compared to other thin film technologies [6]. In particular, the solution-based nature and tunable band gap (1.3-2.3 eV [7]) of perovskite have made it a suitable candidate to be used as top sub-cell in a tandem structure as it is not subject to lattice mismatch constraints which is one of the key issues with existing III-V tandem or III-V on c-Si based tandem solar cells. Efficiencies greater than 30% [8] have already been predicted for two-terminal monolithic and four-terminal mechanical perovskite based tandem solar cells, which are beyond the thermodynamic efficiency limit of single junction c-Si solar cell. The continuously improving temperature coefficient of PSCs for a wide range of temperatures (from -50 ℃ to -10 ℃ [9]) have paved their way to be used as a future technology for space missions.

Along with their positive aspects, the emerging PSCs are currently limited to a number of constraints. Perovskite is hygroscopic by nature; therefore, it tends to absorb moisture from the air that leads to concerns such as efficiency and stability degradation with passage of time [10]. The longest lifetime reported so far for PSCs is one year [11], which is significantly shorter than 25 years as compared to commercialized PV technologies. Further, the

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presence of toxic materials such as lead [12] in perovskite is one of the major concerns holding back the wide-scale deployment of PSC based PV modules. Another major concern is the presence of anomalous hysteresis – the inconsistency in the current-voltage (*J-V*) characteristics between forward and reverse sweep, which makes it difficult to predict the actual efficiency of PSCs [13, 14]. Similarly, the presence of pinholes ─ the nanoscale regions where layer thickness has been completely or partially compromised during the processing, is another concern with existing PSC technology [15]. These concerns are needed to be addressed properly in order to match the current silicon industrial standards and envision the commercialization of PSCs based PV modules.

A number of research groups have explored various techniques to overcome the drawbacks with the existing PSC technology. It was found that the low stability concerns for PSCs can be solved by using high temperature crystal growth processes which result in crystalline grains of millimeter scale [16]. Similarly, the concerns related to pinholes are reported to be minimized using high-purity and large-area growth of perovskite via solution-based hot-casting technique. A number of research groups have also explored various electron transport layers (ETL) [17-20] and hole transport layers (HTL) [21-24] to enhance the efficiency of PSCs. The power conversion efficiency of perovskite/c-Si tandem solar cells has reached 25% experimentally for fully textured surfaces [25]. Furthermore, perovskite based bifacial tandem solar cells have also been investigated under various terminal configurations and the efficiency achieved ~33% at average Earth albedo of 30% [26, 27]. These studies predict the promising potential of PSCs to be widely used as the future PV technology.

In the past, the lead halide perovskite solar cells have been used for large-scale application due to low cost, and excellent photovoltaic performance [28]. However, the lead is very toxic substance that could affect almost every organ in the body at high dose [29]. Research has reported that the lead could leak into environment and also cause water contamination when the solar panel was damaged [30]. In this review, a lot of research efforts have been proposed to replace lead in perovskite solar cells. The physical properties and photovoltaic performance of these lead-free perovskite solar cells were highlighted also.

2 Lead-free perovskite solar cells

Tin based perovskite solar cells

Tin (Sn) is located in the Group 14 in the period table. The tin has been used to replace lead for environmentally benign perovskite [31], due to excellent semiconducting properties. The synthesis of tin halide perovskite nano crystals has been reported by using different methods such as hot injection, chemical vapor deposition and ligand assisted re-precipitation technique [32]. The properties of obtained thin films (thermal stability, chemical, optical, electronic and physical properties) strongly depended on the preparation technique. The power conversion efficiency reached 6% under simulated full sunlight [33] in FTO glass/cp-TiO_2/$CH_3NH_3SnI_3$/spiro-OMeTAD/Au solar cell and the rapid oxidation of Sn^{2+} to be Sn^{4+} could be observed. Researchers point out that addition of antioxidant additives and use low-dimensional structures could reduce tin oxidation [34]. High uniform, pinhole free films and high carrier density in perovskite devices were observed by using dimethyl sulfoxide solution [35]. The band gap values are in the range of 1.2 eV to 1.4 eV [36], allowed light harvesting from the near infrared region [37]. Results showed high open circuit voltage (0.88 V) [38], however, lower values in fill factor (0.48) and short circuit current (21 $mAcm^{-2}$). Yukari and co-workers determined the hole concentration ($9x10^{17}$ cm^{-3}) in conducting $CH_3NH_3SnI_3$ via Hall effect measurement [39]. They explained that artificial hole doping could improve the electrical conductivity without influencing mobility. On the other hand, disadvantages of this type of solar cell were highlighted such as the presence of tin cation (higher toxicity than lead ions) in solar cell, and lower power conversion efficiency if compared to lead based perovskites (low formation energy of tin vacancies [40]). Generally, when the orthorhombic phase has changed to tetragonal phase, caused poor performance in solar cell. Parrott and co-workers [41] have concluded that the charge lifetime is very short at the room temperature under PL measurements. However, recovery of the charge carrier lifetime was observed significantly when the temperature was reduced below the phase transition into the orthorhombic structure near 110 K. Some researchers have mentioned that the $CH_3NH_3SnI_3$ is very unstable in the air. This compound could be partially decomposed within 120 minutes before total decomposition after 24 hours. Based on the experimental findings, Hoshi and co-workers [42] confirmed that addition of 5-ammonium valeric acid iodide can improve the oxidation stability of this compound in the air. Tianyue and co-workers [43] reported the performance of solar cell could be improved by introducing antioxidant gallic acid with $SnCl_2$. This $SnCl_2$-gallic acid complex could protect the perovskite grains and conduct electrons across it. They further explain that this solar cell successfully retains 80% of initial efficiency after 1000 hours in humidity of 20%, and under ambient air conditions. The properties of black orthorhombic form of $CsSnI_3$ were studied. This p-type compound showed near-infrared emission at room temperature with band gap of 1.3 eV [44] and low carrier density. The hole mobility and carrier concentration (at room temperature) were 585 $cm^2/V.s$ and $10^{17} cm^{-3}$, respectively based on the Hall effect measurements [45]. The photovoltaic behaviors showed higher value in Voc (0.42V) and Jcs (4.8 mA/cm^2), however, lower values in power conversion efficacy (0.9%) and fill factor (22%) due to large series resistance and low shunt resistant [46]. Shiyou and co-workers [47] highlighted that $CsSnI_3$ could be used as light absorber materials under moderately Sn-rich conditions. The non-radiative electron hole recombination and electron trapping could be observed in Sn-rich films. In contrast, when the Sn becomes poorer, high concentration of acceptor defects (Cs or Sn vacancies) could be produced easily. The fullerene and CuI were used as n-type and p-type material (hole transport layer), respectively in indium tin oxide (ITO)/copper(I) iodide (CuI)/$CsSnI_3$/fullerene (C_{60})/bathocuproine (BCP)/ aluminium (Al) solar cell. The highest open circuit voltage (Voc) reached 0.55V by using C_{60} as electron extraction layer [48].

Germanium based perovskite solar cells

Germanium halide perovskite is an attractive device due to the well-suited optical properties and non-toxic for photovoltaic applications. It received great attention due to the germanium, which belongs to the same group as tin and showed high absorption coefficients [49] with excellent carrier mobility. Yu-Qing and co-workers [50] reported the electron-hole carrier mobility reached $3.6X10^3$ $cm^2/V.S.$ with excellent absorption coefficients in the full visible spectrum. Indira and co-workers [51] described that power conversion efficiency of $MAGeI_{2.7}Br_{0.3}$ based solar cell achieved 0.57% (adding 10% bromide). The PEDOT:PSS and $PC_{70}BM$ were used as hole and electron transport layer, respectively during the experiment. Kunwu and co-workers [52] highlighted that power conversion efficiencies were 0.11% and 0.2% in $CsGeI_3$ and $CH_3NH_3GeI_3$ absorber materials, respectively. Chenxi and co-workers [53] enhanced photovoltaic performance of solar cell by adding germanium nanoparticles onto mesoporous TiO_2 (served as electron transporting layer) in order to regulate perovskite crystal growth. Scanning electron microscopy (SEM) studies confirmed highly crystalline, highly uniform morphology, and highly coverage layer in the perovskite films onto the mesoporous TiO_2 materials. X-ray diffraction (XRD) measurements supported that higher degree of crystallinity could be observed with increasing of concentration of germanium nanoparticles from 0.2 mg/mL to 1 mg/mL. Results revealed that power conversion efficacy of 18.59 % and the electron mobility were found to be increased over 5 times as the best amount of germanium particles were used. The $CsGeI_3$ based solar cell exhibited excellent photocurrent of 6 $mAcm^{-2}$ [54] and showed cubic structure at room temperature [55]. There are many researchers fabricated methylammonium germanium halide based solar cell and studied photovoltaic parameters of devices as well. Lachgueur and Rahmoun [56] designed solar cell consisted of Al/PEDOT:PSS/$CH_3NH_3GeI_3$-PCBM/FTO. Ahmed and co-workers [57] studied the influence of film thickness on the quality and the performance of solar cells. The best thickness was 600 nm based on research findings. The power conversion efficiency of 21% could be reached when the hole transport materials were Cu_2O and D-PBTTT-14. Other hole transport materials [58] including NiO, CuI, Spiro-OMeTAD and PEDOT-PSS showed different Jsc (13.91 to 14.78 mA/cm^2), Voc (0.97 to 1.93 V), fill factor (68.76% to 86.97%) and power conversion efficiency values (12.35 % to 20.05%). Nacereddine and Hima [59] have reported performance of solar cell was improved after adding C_{60} as electron transport material (efficiency=13.5%). Arnob and co-workers [60] employed zinc oxide and nickel oxide (metal oxide transport layer) during the experiment. Power conversion efficiency about 8% could be obtained when the thickness was 800 nm. Laszlo and co-workers [61] synthesized various types of three-dimensional structures such as $CsGeI_3$, $CH_3NH_3GeI_3$, $HC(NH_2)_2GeI_3$ and $CH_3C(NH_2)_2GeI_3$ with the band gap of 1.6 eV, 1.9 eV, 2.2 eV and 2.5 eV, respectively. Also, other one-dimensional compounds including $C(NH_2)_3GeI_3$, $(CH_3)_3NHGeI_3$ and $(CH_3)_2C(H)NH_3GeI_3$ have been produced and indicated band gap of 2.7eV, 2.5 eV and 2.8 eV, respectively. Sun and co-workers [62] point out that optical properties, band gap, stability, hole and electron conductive behaviors of the $MAGeI_3$ materials analogues to the $MAPbI_3$ compounds. On the other hand, the disadvantages of this solar cell were reported. The main issue was chemically instability upon oxidation of the divalent germanium cation (oxidation from (II) to (IV)). Generally, the highest stability of the 2+ oxidation state could be observed in lead if compared to germanium [63]. Liang and co-workers [64] reported germanium based two-dimensional Ruddkesden-Popper hybrid perovskite indicated desirable light absorption properties with the band gap value from 2 eV to 2.5 eV. They found that thermodynamic stability of solar cell could be improved with a thickness of few tens of unit cells.

Bismuth based perovskite solar cells

Low toxic bismuth based perovskites have been synthesized to replace lead perovskite solar cells [65]. Oz and co-workers [66] designed ITO/PEDOT:PSS/$(CH_3NH_3)_3Bi_2I_9$/PCBM/Ca/Al solar cell with the power conversion efficiency about 0.07%. The obtained compound showed hexagonal structure with orientation along the c-axis, band gap about 2.9 eV and photoluminescence emission at 751 nm. On the other hand, Ajay and co-workers [67] revealed three diffraction peaks at 8.16, 16.34 and 24.62 corresponded to (002), (004) and (006) planes in the XRD studies. Further, this compound showed a peak at 500 nm based on the UV-Vis spectra. SEM analysis revealed that star shape and hexagonal morphology could be observed in NiO film and TiO_2 layer, respectively. Power conversion efficiency, Jsc, Voc and fill factor were observed to be 0.22%, 0.4 mA/cm^2, 0.64V and 0.81, respectively. Several techniques have been used to produce bismuth based thin films as reported. Experimental results supported that photoluminescence decay times to be 760 ps, which is considered as longer times in vapor processing if compared to solution processing. XRD patterns confirmed different dominating crystal growth directions could be observed in the solution processed $CsBi_3I_{10}$ perovskite thin films [68] than other deposition methods. The band gap value was 1.77

eV and photocurrent up to 700 nm. Solar cell was fabricated from different hole transporting materials as reported [69]. Higher power conversion efficiency could be found in the poly(3-hexylthiophene-2,5-diyl) (1.62%) if compared to spiro-OMeTAD (1.12%). XRD analysis exhibited hexagonal phase, (P1211) space group and single crystalline structure. The iodine 3d and Bi 4f core level peak could be observed in 620 nm and 158 eV, respectively as shown in X-ray photoelectron spectroscopy studies. Chunfeng and co-workers [70] synthesized formamidinium based bismuth perovskite and showed hexagonal phase, with the band gap of 2.19 eV and exciton binding energy of 260 meV. The power conversion efficiency about 0.022% with the highest open voltage (0.48V) could be observed. Mehri and co-workers [71] developed phenethylammonium bismuth halide solar cell, which successfully exhibited good thermal and humidity stability. The Jsc, Voc and power conversion efficiency were observed to be 0.81 mA/cm^2, 614 mV and 0.3%, respectively. The $Cs_3Bi_2I_9$ has lower power conversion efficiency because of indirect transition and larger band gap value (2.2 eV). Yu and co-workers [72] fabricated $Cs_3Bi_2I_6Br_3$ solar cell during the experiment. The photovoltaic parameters (power conversion efficiency=1.15%, Jsc=3.11 mA/cm^2, Voc=650 mV) and unique behaviors (high crystallinity, band gap=2.03 eV) were reported. On the other hand, the disadvantages of this type of solar cells were highlighted including very poor surface morphology, and seriously caused poor performance of solar cells [73]. Fabrication of bulk hetero-junction perovskite by using $Ag_3Bi_2I_9$ and $Cs_3Bi_2I_9$ compounds [74] has been reported in an attempt to improve solar cell efficiency. Finally, solar cell achieved power conversion efficiency of 3.6% with open circuit voltage about 0.89V. The obtained solar cells showed excellent thermal stability, successfully retained about 90% of the initial efficiency in glove box, under 85 °C after 450 hours.

Antimony based perovskite solar cells

The antimony (Sb) based perovskite solar cells showed non-toxic, extremely cheap, excellent intrinsic thermodynamic stability and unique optoelectronic behaviors [75]. Hebig and co-workers [76] produced the solar cell ($ITO/PEDOT:PSS/(CH_3NH_3)_3Sb_2I_9/PCBM/ZnO/Al$), indicated power conversion efficiency of 0.49%. The methylammonium antimony iodide compound was synthesized by using solution based method. The band gap was 2.14 eV and absorption coefficient value to be 10^5 cm^{-1}. Based on the XRD data [77], there are four diffraction peaks at 8.22, 16.54, 24.88 and 50.98, attributed to the (001), (002), (003) and (402) planes, respectively. The UV-visible spectrum displayed very strong peak at 460 nm in the $(CH_3NH_3)_3Sb_2I_9$ compound. The scanning electron microscope (SEM) images showed hexagonal structure when the films were grown on TiO_2 and NiO layer. Photovoltaic behaviors of solar cell including efficiency (0.08%), Jsc (0.25 mA/cm^2), Voc (0.45 V) and fill factor (0.7) were reported. The disadvantages of this type solar cell were uncontrollable halide constituents, disorder of the growth process and very poor film morphology. Yi and co-workers [78] produced high quality of $MA_3Sb_2I_{9-x}Cl_x$ films by adding bis(trifluoromethane)sulfonamide lithium, in order to improve the heterogeneous nucleation. The power conversion efficiency was 3.34%, and successfully retained 90% of the initial efficacy after 1400 hours under ambient conditions. Khursheed and co-workers [79] designed $FTO/CL\text{-}TiO_2/m\text{-}TiO_2/MASbI/HTM/Au$ solar cell and showed the highest open circuit voltage of 740 mV. Praveen and co-workers [80] have synthesized absorber material ($(NH_4)_3Sb_2I_9$) by using two step deposition procedures. The solar cell consisted of $FTO/CL\text{-}TiO_2/m\text{-}TiO_2/(NH_4)_3Sb_2I_9/HTM/Au$ was reported, and indicated open circuit voltage of 945 mV with power conversion efficiency achieved 0.42%. On the other hand, study of structural properties of $(CH_3NH_3)_3Sb_2I_9$ was reported by Jakubas and co-workers [81], whereas investigation of the phase transition of $Cs_3Sb_2I_9$ was carried out by Bagautdinov and co-workers [82]. The $(NH_4)_3Sb_2I_9$ compound was produced by using ethanol [83]. The properties of compound (band gap=2.27eV, power conversion efficiency=0.51%, open circuit voltage=1.03 V, hole mobility= 4.8 cm^2/V.s, electron mobility=12.3 cm^2/V.s) were highlighted. Formation of stoichiometric antimony based compound has been proposed by Boopathi and co-workers [84]. The band gap and power conversion efficiency were found to be 1.95eV and 2.04%, respectively. Buonassisi and co-workers [85] have prepared different solution processed antimony based compounds. The $Cs_3Sb_2I_9$ compound showed indirect band gap (2.43 eV), the largest exciton binding energy (175 meV) and the lowest photo current (0.13 mA/cm^2). The $Rb_3Sb_2I_9$ compound exhibited direct band gap (2.03 eV), the lowest exciton binding energy (101 meV), the highest photocurrent (1.67 mA/cm^2) and has 2-dimensional structure. The $K_3Sb_2I_9$ compound indicated intermediate exciton binding energy (129 meV), intermediate photo current (0.4 mA/cm^2) and band gap about 2.02 eV.

Copper based perovskite solar cells

The nontoxic copper metal could be used to replace lead in the perovskite solar cell. The copper based perovskite solar cell showed suitable band gap and tuning of the optical absorption from visible to near-infrared range [86]. The highest power conversion efficiency (21.76%) with fill factor of 85%, Jsc of 23.26 mA/cm^2 and Voc of 1.1V could be observed in $(CH_3NH_3)_2CuCl_4$ compound if compared to others. The band gap and affinity were found to be 0.99 eV and 3.9, respectively in $(CH_3NH_3)_2CuCl_2I_2$. The binding energy, isolated energy, electronic energy and heat of formation were observed to be -345.53 kcal/mol, -1423.56 kcal/mol, -10735.65 kcal/mol and -3.6 kcal/mol, respectively in $(CH_3NH_3)_2CuCl_2Br_2$ compound. Research findings showed several p-type inorganic copper based hole transport layer materials were chemically stable and economical [87]. These materials showed unique physical properties including high conductivity, high hole mobility, excellent transmittance and suitable energy levels. Several copper substituted lead perovskite compounds were reported as indicated in Table 1.

Table 1: Several copper substituted lead perovskite compounds were prepared under various deposition methods

Compound	Deposition method	Highlighted results
CuSCN	Spin coating, doctor blade technique, SILAR method and electro deposition method	Band gap=3.8 eV
CuSeCN	Spin coating technique	Band gap=3.1 eV. Materials exhibited nanocrystalline, yield hole mobility of 0.002 $cm^2/V.s$ and optically transparent more than 94% [88]
CuI	Spin coating, doctor blading, spray deposition, chemical bath deposition, thermal evaporation, electro chemical technique, chemical extraction method	High transparency, high hole mobility, excellent chemical stability, low production cost and band gap of 3.1 eV
$CuGaO_2$	Drop casting, spray pyrolysis, spin coating and pulsed laser deposition	Fill factor, short circuit current density, open circuit voltage and power conversion efficiency were 0.68, 20.9 mW/cm^2, 1.04 V and 14.7%, respectively. Band gap=3.6 eV [89]
$CuCrO_2$	Spin coating, chemical solution deposition, spray deposition and reactive magnetron sputtering method	Band gap = 3.3 eV
$CuAlO_2$	Vacuum sputter, DC sputtering, pulsed laser deposition, RF magnetron sputtering and chemical solution deposition	Band gap =4.5 eV
CuO, Cu_2O	SILAR method, electrospray technique, spin coating and electro deposition method	Band gap of 1.3 eV and 2.2 eV for CuO and Cu_2O, respectively. Monoclinic phase and cubic phase in cupric oxide (CuO) and cuprous oxide (Cu_2O), respectively based on the XRD data. The ultrathin Cu_2O could be used to produce high performance of devices with the power conversion efficiency of 11%. The Cu_2O showed high hole mobility, excellent energy level and longer life time of photo excited carriers [90]

The spin coating method was employed for the production of CuO film. Morphology studies revealed big grain, pinhole-free structure and compact in the obtained films. The best power conversion efficiency was 17.43% in ITO/CuO/MAPbI3/PC61BM/ZnO/Al solar cell. CuO film could be considered as excellent hole transporting material if compared to PEDOT:PSS (efficiency=11.98%) under same experimental conditions [91]. Mansoura and co-workers [92] synthesized one-dimensional copper chloride perovskite at room temperature under slow evaporation technique. The band gap was 2.56 eV, and showed monoclinic space group $P2_1/n$. Based on the TG-DTA studies, the obtained materials were very stable in ambient temperature, indicated endothermic phase transition when the temperature was 83 °C. Daniele and co-workers [93] demonstrated the preparation of 2-dimensional $(CH_3NH_3)_2CuCl_xBr_{4-x}$ materials. Experimental results confirmed the absorption could be extended to near-infrared region, and formation of copper (I) ions could be observed for green photoluminescence. The $(NH_3C_3H_6NH_3)CuBr_4$ was produced via spin coating method by using solvent (DMSO) [94]. This compound showed dense, flexible and band gap about 1.7 eV. The grain sizes were in the range of 200 to 400 nm and film roughness was 36 nm, respectively based on the SEM and AFM studies. XRD studies confirmed the monoclinic structure and the major peaks could be observed at 10.06°, 16.21°, 26.3°, 30.5°, 32.6° and 41.3°. The conductivity, carrier mobility, and carrier concentration were 89.3 S/cm, $1.95X10^{-1}$ $cm^2/V.s$, and $1.28X10^{16}$ cm^{-3}, respectively.

Cesium based perovskite solar cells

The researcher has reported that $Cs_2AgBiBr_6$ compound could be used to produce lead free solar cell. The lead element was replaced successfully by silver (Ag^+) cation and bismuth ions (Bi^{3+}) in the crystal lattice. High quality of $Cs_2AgBiBr_6$ compound (band gap=4.2 eV) was proposed by Cuncun and co-workers [95] via low pressure assisted solution method. The solar cell consisted of Au/P3HT/$Cs_2AgBiBr_6$/SnO_2/ITO showed the power conversion efficiency about 1.44%. Grain size of 0.5 µm of $Cs_2AgBiBr_6$ was synthesized through one step spin coating deposition technique [96] by using dimethyl sulfoxide-N,N-dimethylformamide mixture. Experimental findings confirmed that high quality of compound could be obtained and the power conversion efficiency was more than 1%.

Maximillian and co-workers [97] synthesized the 2-D/3D $Cs_2AgBiBr_6$ double perovskite solar cells by using phenethyl ammonium (served as the constituting cation). Experimental results point out that the highest power conversion efficiency and Voc are 2.5% and 1.18 V, respectively. Guan and c-workers [98] produced the $Cs_2SnI_{6-x}Br_x$(x=0-6) via chemical solid solution method. The obtained compounds showed cubic structure with symmetry of Fm3m based on the XRD studies. The band gap energy (1.25 eV to 3.01 eV), and thermal stability increased with increasing the bromine content as reflected in UV/Vis spectral and thermos gravimetric analysis, respectively. Several indoline dyes were added to the TiO_2 electron transport layer during the experiment. The single source evaporation deposition technique was used to prepare the $Cs_2AgBiBr_6$ compound [99]. The SEM and XRD studies revealed that flat morphology, pinhole free structure and high crystallinity phase in annealed films for 15 minutes and at 300 °C. The solar cell made from FTO/compact TiO_2/$Cs_2AgBiBr_6$/spiro-OMeTAD/Ag, showed power conversion efficiency of 0.7%, fill factor of 0.65, Voc of 0.87V and Jsc of 1.24 mA/cm^2. The pulsed laser deposition was employed for the synthesis of high quality halide perovskite compound [100]. The stoichiometric compound could be achieved with the grain size more than 200 nm. Femi and co-workers [101] produced $Cs_2AgBiBr_6$ compounds through the vacuum sublimation method and solution processing technique. Research findings confirmed that narrower band gap value, good composition stoichiometric, excellent crystallinity, higher mobility and longer photo excitation lifetime could be observed in solution processed films. The highest power conversion efficiency successfully reached 2.5% as well. Big grains and very smooth surface morphologies were observed in high quality perovskite films which produced by using sequential vapor deposition method [102]. Greul and co-workers [103] concluded that high annealing temperature is needed to provide the best conditions for preparing the $Cs_2AgBiBr_6$ films. The obtained films reached the power conversion efficiency of 2.5% with Voc value more than 1.0 V. On the other hand, $Cs_2AgInCl_6$ compounds have attracted great attention due to dopant induced photo luminescence and self-trapped exciton emission [104]. SEM studies revealed that as-prepared films consisted of regular rhombic dodecahedral particles and average grain sizes could be observed in the range of 5 µm to 12 µm [105]. Thermogravimetric and differential scanning calorimetry demonstrated that the obtained materials were very stable at 400 °C, then, decomposition reaction occurred. Based on the PL measurement, red emission band could be detected at 635 nm, corresponding to the photo-induced defects in compounds. Weihua eco-workers [106] point out high crystal quality grains could be found, and the diameters equals to film thickness as well, indicating to minimize the grain boundary length. Experimental results showed power conversion efficiency more than 1% and very long electron hole diffusion lengths (more than 100 nm). The properties of $CsMnCl_3$ perovskites were described by Sozen and co-workers [107]. Structural characterization confirmed this compound formed cubic phase. Optical properties revealed the band gap of 4.1 eV with an indirect transition. Experimental results showed robust antiferromagnetic order. The Cs_2SnI_6 showed cubic phase and the space group Fm-3m(225). Raman spectroscopy technique indicated green laser at 514.4 nm, due to this compound adsorbed the visible region [108].

3. Conclusions

In recent times, perovskite solar cell has emerged as important technology to generate electricity. As per literature, the properties and photovoltaic performance of fabricated solar cells depended onto various experimental conditions. Herein, this review offers a comprehensive insight into the preparation of perovskite solar cells by using tin, germanium, bismuth, copper, cesium and antimony. Research findings indicated excellent absorption coefficient in tin-based perovskites, while Bi-based and Sb-based perovskites showed very stable conditions. Lastly, the performance of lead-free perovskites should be improved from time to time in order to achieve the needs of commercial development.

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References

[1] K. Yoshikawa, H. Kawasaki, W. Yoshida, T. Irie, K. Konishi, K. Nakano, K. Yamamoto, Silicon heterojunction solar cell with interdigitated back contacts for a photoconversion efficiency over 26%, *Nat. Energy*, **2**, 1-8 (2017).

[2] A. Polman, M. Knight, C. Garnett, B. Ehrler, W. Sinke, Photovoltaic materials: present efficiencies and future challenges, *Science*, **352**, DOI: 10.1126/science.aad4424 (2016).

[3] A. Green, A. Ho, H. Snaith, The emergence of perovskite solar cells, *Nat. Photonics*, **8**, 506-514 (2014).

[4] NREL, "Best research-cell efficiency chart". https://www.nrel.gov/pv/cell-efficiency.html.

[5] G. Xing, N. Mathews, S. Lim, N. Yantara, X. Liu, T. Sum, Low-temperature solution-processed wavelength-tunable perovskites for lasing, *Nat. Mater*., **13**, 476-480 (2014).

[6] U. Qasim, M. Saeed, H. Imran, Optimization of various terminal topologies of bifacial perovskite/$FeSi_2$ tandem solar cell, *Jpn. J. Appl. Phys*., https://doi.org/10.35848/1347-4065/ac26e3 (2021).

[7] E. Unger, L. Kegelmann, K. Suchan, D. Sörell, L. Korte, S. Albrecht, Roadmap and roadblocks for the band gap tunability of metal halide perovskites, *J. Mater. Chem. A*, **5**, 11401-11409 (2017).

[8] M. Filipič, P. Löper, B. Niesen, C. Ballif, M. Topič, $CH_3NH_3PbI_3$ perovskite/silicon tandem solar cells: characterization based optical simulations, *Opt. Express*, **23**, A263-A278 (2015).

[9] F. Wang, Z. Qiu, Y. Chen, Y. Zhang, N. Li, H. Zhou, Temperature-insensitive efficient inorganic perovskite photovoltaics by bulk heterojunctions, *Adv. Mater.*, https://doi.org/10.1002/adma.202108357 (2022).

[10] S. Zhang, G. Han, Intrinsic and environmental stability issues of perovskite photovoltaics, *Prog. Energy*, https://doi.org/10.1088/2516-1083/ab70d9 (2020).

[11] G. Grancini, C. Roldán, I. Zimmermann, E. Mosconi, D. Martineau, K. Nazeeruddin, One-year stable perovskite solar cells by 2D/3D interface engineering, *Nat. Commun.*, **8**, 1-8 (2017).

[12] A. Djurišić, Z. Liu, H. Tam, K. Wong, B. He, Perovskite solar cells-An overview of critical issues, *Prog. Quantum Electron*, **53**, 1-37 (2017).

[13] U. Qasim, B. Qasim, M. Saeed, H. Riaz, H. Imran, Investigating physical origin of dominant hysteresis phenomenon in perovskite solar cell, *J. Mater. Sci. Mater. Electron*, **32**, 5274-5285 (2021).

[14] W. Tress, N. Marinova, T. Moehl, M. Zakeeruddin, K. Nazeeruddin, M. Grätzel, Understanding the rate-dependent J–V hysteresis, slow time component, and aging in $CH_3NH_3PbI_3$ perovskite solar cells: the role of a compensated electric field, *Energy Environ. Sci.*, **8**, 995-1004 (2015).

[15] S. Ghosh, S. Mishra, T. Singh, Antisolvents in perovskite solar cells: importance, issues, and alternatives, *Adv. Mater. Interfaces*, https://doi.org/10.1002/admi.202000950 (2020).

[16] W. Nie, H. Tsai, R. Asadpour, J. Blancon, G. Gupta, A. Mohite, High-efficiency solution-processed perovskite solar cells with millimeter-scale grains, *Science*, **347**, 522-525 (2015).

[17] H. Li, W. Shi, W. Huang, E. Yao, Y. Yang, Carbon quantum dots/TiO_x electron transport layer boosts efficiency of planar heterojunction perovskite solar cells to 19%, *Nano Lett.,* **17**, 2328-2335 (2017).

[18] X. Gao, J. Li, S. Gollon, M. Qiu, C. Yuan, A TiO_2 nanotube network electron transport layer for high efficiency perovskite solar cells, *Phys.Chem. Chem. Phys.*, **19**, 4956-4961 (2017).

[19] K. Cao, J. Cui, H. Zhang, H. Li, M. Wang, Efficient mesoscopic perovskite solar cells based on the $CH_3NH_3PbI_2Br$ light absorber, *J. Mater. Chem. A*, **3**, 9116-9122 (2015).

[20] J. You, Z. Hong, Y. Yang, Q. Chen, Y. Yang, Low-temperature solution-processed perovskite solar cells with high efficiency and flexibility, *ACS Nano*, **8**, 1674-1680 (2014).

[21] H. Noh, N. Jeon, C. Choi, K. Nazeeruddin, S. Seok, Nanostructured TiO_2/$CH_3NH_3PbI_3$ heterojunction solar cells employing spiro-OMeTAD/Co-complex as hole-transporting material, *J. Mater. Chem. A*, **1**, 11842-11847 (2013).

[22] J. Jeon, H. Noh, Y. Kim, W. Yang, S. Seok, Solvent engineering for high-performance inorganic–organic hybrid perovskite solar cells, *Nat. Mater.*, **13**, 897-903 (2014).

[23] Y. Zhang, W. Liu, F. Tan, Y. Gu, The essential role of the poly (3-hexylthiophene) hole transport layer in perovskite solar cells, *J. Power Sources*, **274**, 1224-1230 (2015).

[24] B. Jheng, P. Chiu, S. Yang, Y. Tong, Using $ZnCo_2O_4$ nanoparticles as the hole transport layer to improve long term stability of perovskite solar cells, *Sci. Rep.*, https://doi.org/10.1038/s41598-022-06764-w (2022).

[25] F. Sahli, J. Werner, A. Kamino, M. Bräuninger, C. Ballif, Fully textured monolithic perovskite/silicon tandem solar cells with 25.2% power conversion efficiency, *Nat. Mater.*, **17**, 820-826 (2018).

[26] H. Imran, I. Durrani, M. Kamran, M. Abdolkader, Z. Butt, High-performance bifacial perovskite/silicon double-tandem solar cell, *IEEE J. Photovolt.*, **8**, 1222-1229 (2018).

[27] R. Asadpour, R. Chavali, K. Ryyan, M. Alam, Bifacial Si heterojunction-perovskite organic-inorganic tandem to produce highly efficient (π_T^*~33%) solar cell, *Appl. Phys. Lett.*, https://doi.org/10.1063/1.4922375 (2015).

[28] S.M. Ho, I. Paulraj, M. Kumar, R. Sonker, P. Nandi. Recent developemnts on the proeprties of chalcogenide thin films. In: D. Vikraman, editor. Chalcogens. 1st ed. London: IntechOpen; DOI: 10.5772/intechopen.102429. (2022).

[29] C. Lin, Stabilizing organic–inorganic lead halide perovskite solar cells with efficiency beyond 20%, *Front. Chem.*, https://doi.org/10.3389/fchem.2020.00592 (2020).

[30] Y. Chen, X. Liu, T. Wang, Y. Zhao, Highly stable inorganic lead halide perovskite toward efficient photovoltaics, *Acc. Chem. Res.*, **54**, 3452-3461 (2021).

[31] C. Jiupeng, F. Yan, Recent progress in tin-based perovskite solar cells, *Energy Environ. Sci.*, **14**, 1286-1325 (2021).

[32] S. Naoto, B. Zhang, J. Chen, M. Osman, H. Sun, F. Omar, Advances and challenges in tin halide perovskite nanocrystals, *ACS Mater. Lett.*, **3**, 1541-1557 (2021).

[33] H. Feng, C. Stoumpos, H. Cao, H. Chang, K. Mercouri, Lead free solid state organic inorganic halide perovskite solar cells, *Nat. Photonics*, **8**, 489-494 (2014).

[34] J. Xianyuan, Z. Zang, Y. Zhou, H. Li, Z. Ning, Tin halide perovskite solar cells: an emerging thin-film photovoltaic technology, *Acc. Mater. Res.*, **2**, 210-219 (2021).

[35] F. Hao, C. Stoumpos, K. Mercouri, N. Zhou, P. Guo, H. Chang, Solvent-mediated crystallization of $CH_3NH_3SnI_3$ films for heterojunction depleted perovskite solar cells, *J. Am. Chem. Soc.*, **137**, 11445-11452 (2015).

[36] M. Tech, L. Leong, P. Boix, C. Andrew, K. Thirumal, Formamidinium tin-based perovskite with low E_g for photovoltaic applications, *J. Mater. Chem. A*, **3**, 14996-15000 (2015).
[37] C. Constantinos, D. Christos, K. Mercouri, Semiconducting tin and lead iodide perovskites with organic cations: phase transitions, high mobilities, and near-infrared photoluminescent properties, *Inorg. Chem*., **52**, 9019-9038 (2103).
[38] K. Nakita, D. Samuel, A. Abate, W. Christian, Lead-free organic–inorganic tin halide perovskites for photovoltaic applications, *Energy Environ. Sci*., **7**, 3061-3068 (2014).
[39] T. Yukari, H. Hiroyuki, T. Yukihiro, T. Inabe, Hall mobility in tin iodide perovskite $CH_3NH_3SnI_3$: evidence for a doped semiconductor, *J. Solid State Chem*., **205**, 39-43 (2013).
[40] M. Mottakin, K. Sobayel, D. Sarkar, A. Hend, A. Sami, T. Kuaanan, S. Md, N. Amin, K.Sopian, Desgin and modelling of eco-friendly $CH_3NH_3SnI_3$ based perovskite solar cells with suitable transport layers, *Energies*, https:// doi.org/10.3390/en14217200 (2021).
[41] S. Parrott, L. Milot, S. Thomas, J. Henry, B. Michael, Effect of structural phase transition on charge-carrier lifetimes and defects in $CH_3NH_3SnI_3$ perovskite, *J. Phys. Chem. Lett*., **7**, 1321-1326 (2016).
[42] H. Hoshi, T. Dai, S. Naoyuki, Improved oxidation stability of tin iodide cubic perovskite treated by 5-ammonium valeric acid iodide, *Mater. Lett*., **183**, 391-393 (2016).
[43] W. Tianyue, Q. Tai, X. Guo, J. Cao, C. Liu, F. Yan, Highly air-stable tin-based perovskite solar cells through grain-surface protection by gallic acid, *ACS Energy Lett*., **5**, 1741-1749 (2020).
[44] K. Mulmudi, D. Sabba, W. Leong, P. Boix, Lead-free halide perovskite solar cells with high photocurrents realized through vacancy modulation, *Adv. Mater*., **26**, 7122-7127 (2014).
[45] C. In, J. Song, J. Im, H. Li, F. Arthur, A. John, $CsSnI_3$: semiconductor or metal? High electrical conductivity and strong near-infrared photoluminescence from a single material. High hole mobility and phase-transitions, *J. Am. Chem. Soc*., **134**, 8579-8587 (2012).
[46] C. Zhuo, J. Jian, Y. Ren, C. Yu, S. Kai, Schottky solar cells based on CsSnI3 thin films, *Appl. Phys. Lett*., **101**, DOI: 10.1063/1.4748888 (2012).
[47] C. Shiyou, X. Peng, H. Xiang, X. Gong, S. Wei, Influence of defects and synthesis conditions on the photovoltaic performance of perovskite semiconductor $CsSnI_3$, *Chem. Mater.,* **26**, 6068-6072 (2014).
[48] P. Kenneth, I. Walton, A. Ross, Tin perovskite/fullerene planar layer photovoltaics: improving the efficiency and stability of lead-free devices, *J. Mater. Chem. A*, **3,** 11631-11640 (2015).
[49] Y. Dexin, G. Zhang, R. Lai, C. Yao, Y. Lian, M. Rao, B. Zhao, Germanium-lead perovskite light-emitting diodes, *Nat. Commun*., **12**, https://doi.org/10.1038/s41467-021-24616-5 (2021).
[50] Z. Yu, B. Liu, M. Cai, D. Cao, Tuning charge carrier types, superior mobility and absorption in lead-free perovskite $CH_3NH_3GeI_3$: theoretical study, *Electrochim. Acta*, **247**, 891-898 (2017).
[51] K. Indira, F. Bastian, H. Sebastian, K. Birgit, T. Gregor, Enhanced performance of germanium halide perovskite solar cells through compositional engineering, *ACS Appl. Energy Mater*., **1**, 343-347 (2018).
[52] F. Kunwu, Y. Anita, H. Kumar, T. Pham, *Germanium based perovskites*, in Perovskite solar cells: Technology and practices, 1st ed., Apple Academic Press: New York, (2019).
[53] Z. Chenxi, Z. Li, X. Deng, B. Yan, Z. Wang, S. Huang, Enhancing photovoltaic performance of perovskite solar cells utilizing germanium nanoparticles, *Sol. Energy*, **188**, 839-848 (2019).
[54] T. Krishnamoorthy, H. Ding, S. Mhaisalkar, A. Mark, M. Sherburne, Lead-free germanium iodide perovskite materials for photovoltaic applications, *J. Mater. Chem. A*, **3**, 23829-23832 (2015).
[55] W. Riley, C. Ni, G. Dylan, Y. He, T. Victor, Exploring structural nuances in germanium halide perovskites using solid-state ^{73}Ge and ^{133}Cs NMR spectroscopy, *J. Phys. Chem. Lett*., **13**, 1687-1696 (2022).
[56] A. Lachgueur, K. Rahmoun, *Simulation and analysis of perovskite solar cell based on germanium*, in ICREEC 2019. Springer Proceedings in Energy. Springer:Singapore (2020).
[57] A. Ahmed, B. Kanoun, A. Merad, G. Souraya, Toward development of high-performance perovskite solar cells based on $CH_3NH_3GeI_3$ using computational approach, *Sol. Energy*, **182**, 237-244 (2019).
[58] K. Deepak, D. Kumar, D. Rawat, A diverse outlook on the performance of perovskite solar cells to meet the energy demand, *Int. J. Renew. Energy Res*., **11**, 1811-1821 (2021).
[59] L. Nacereddine, A. Hima, Electron transport material effect on performance of perovskite solar cells based on $CH_3NH_3GeI_3$, *Opt. Mater*., https://doi.org/10.1016/j.optmat.2019.109517 (2020).
[60] G. Arnob, D. Shahriyar, S. Nikor, S. Nazmus, S. Arnob, Performance analysis of an efficient and stable perovskite solar cell and a comparative study of incorporating metal oxide transport layers, *J. Opt. Soc. Am. B*, **37**, 1966-1973 (2020).
[61] F. Laszlo, J. Clark, S. Kim, H. Rhim, J. Arthur, J. Jang, C. Stoumpos, Hybrid germanium iodide perovskite semiconductors: active lone pairs, structural distortions, direct and indirect energy gaps, and strong nonlinear optical properties, *J. Am. Chem. Soc*., **137**, 6804-6819 (2015).
[62] P. Sun, Q. Li, L. Yang, Z. Li, Theoretical insights into a potential lead-free hybrid perovskite: substituting Pb^{2+} with Ge^{2+}, *Nanoscale*, **8**, 1503-1512 (2016).

[63] D. Umadevi, W. Watson, Quasiparticle GW calculations on lead-free hybrid Ge iodide perovskite $CH_3NH_3GeI_3$ for photovoltaic applications, *ACS Omega,* **4**, 5661-5669 (2019).

[64] M. Liang, M. Ju, J. Dai, X. Zeng, Tin and germanium based two-dimensional Ruddlesden–Popper hybrid perovskites for potential lead-free photovoltaic and photoelectronic applications, *Nanoscale*, **10**, 11314-11319 (2018).

[65] B. Park, P. Bertrand, X. Zhang, R. Hakan, B. Gerrit, Bismuth based hybrid perovskites $A_3Bi_2I_9$ (A: Methylammonium or Cesium) for solar cell application, *Adv. Mater*., **27**, 6806-6813 (2015).

[66] S. Oz. J. Hebig, E. Jung, M. Paul, Zero-dimensional $(CH_3NH_3)_3Bi_2I_9$ perovskite for optoelectronic applications, *Sol. Energy Mater. Sol. Cells*, **158**, 195-2015 (2016).

[67] K. Ajay, .M. Hideaki, K. Hiroshi, Y. Kouji, Lead-free perovskite solar cells using Sb and Bi-based $A_3B_2X_9$ and A_3BX_6 crystals with normal and inverse cell structures, *Nano Converg*., https://doi.org/10.1186/s40580-017-0120-3 (2017).

[68] B. Malin, H. Zhu, J. Erik, Extended photo-conversion spectrum in low-toxic bismuth halide perovskite solar cells, *J. Phys. Chem. Lett.,* **7**, 3467-3471 (2016).

[69] M. Jain, T. Edvinsson. R. Durrant, Green fabrication of stable lead-free bismuth based perovskite solar cells using a non-toxic solvent, *Commun. Chem*., https://doi.org/10.1038/s42004-019-0195-3 (2019).

[70] L. Chunfeng, G. Liang, H. Lan, H. Peng, D. Zhang, H. Sun, P. Fan, Lead-free formamidinium bismuth perovskites $(FA)_3Bi_2I_9$ with low bandgap for potential photovoltaic application, *Sol. Energy,* **177**, 501-507 (2019).

[71] G. Mehri, M. Hao, D. He, M. Lyu, Y. Bai, P. Chen, L. Wang, Phenethylammonium bismuth halides: from single crystals to bulky-organic cation promoted thin-film deposition for potential optoelectronic application, *J. Mater. Chem. A*, **7**, 20733-20741 (2019).

[72] B. Yu, M. Liao, J. Yang, W. Chen, Y. Zhu, S. Wei, X. Zhang, Alloy-induced phase transition and enhanced photovoltaic performance: the case of $Cs_3Bi_2I_{9-x}Br_x$ perovskite solar cells, *J. Mater. Chem. A*, **7**, 8818-8825 (2019).

[73] K. Ahmad, *Bismuth halide perovskites for photovoltaic applications*, in Bismuth-fundamentals and optoelectronic applications, IntechOpen: London (2020).

[74] H. Wanpei, X. He, M. Zhang, T. Chen, Y. Lu, L. Zhang, X. Li, Bulk heterojunction gifts bismuth-based lead-free perovskite solar cells with record efficiency, *Nano Energy*, https://doi.org/10.1016/j.nanoen.2019.104362 (2020).

[75] J. Zhixin, Z. Zhang, Z. He, H. Song, G. Teresa, A critical review on bismuth and antimony halide based perovskites and their derivatives for photovoltaic applications: recent advances and challenges, *J. Mater. Chem. A*, **8**, 16166-16188 (2020).

[76] J. Hebig, I. Kuhn, F. Jan, K. Thomas, Optoelectronic properties of $(CH_3NH_3)_3Sb_2I_9$ thin films for photovoltaic applications, *ACS Energy Lett*., **1**, 309-314 (2016).

[77] K. Ajay, M. Hideaki, H. Sugita, H. Kanda, S. Kanaya, S. Ito, Lead-free perovskite solar cells using Sb and Bi-based $A_3B_2X_9$ and A_3BX_6 crystals with normal and inverse cell structures, *Nano Converg*., https://doi.org/10.1186/s40580-017-0120-3 (2017).

[78] Y. Yi, L. Cheng, M. Cai, Y. Liao, Y. Ding, S. Ma, S. Dai, Dimension-controlled growth of antimony-based perovskite-like halides for lead-free and semitransparent photovoltaics, *ACS Appl. Mater. Interfaces*, **12**, 17062-17069 (2020).

[79] A. Khursheed, P. Kumar, M. Mobin, A two-step modified sequential deposition method-based Pb-free $(CH_3NH_3)_3Sb_2I_9$ perovskite with improved open circuit voltage and performance, *ChemElectroChem*, **7**, 946-950 (2020).

[80] K. Praveen, K. Ahmad, J. Dagar, U. Eva, S. Mobin, Two-step deposition approach for lead free $(NH_4)_3Sb_2I_9$ perovskite solar cells with enhanced open circuit voltage and performance, *ChemElectroChem*, **8**, 3150-3154 (2021).

[81] R. Jakubas, R. Decressain, J. Lefebvre, NMR and dilatometric studies of the structural phase transitions of $(CH_3NH_3)_3Sb_2I_9$ and $(CH_3NH_3)_3Bi_2I_9$ crystals, *J. Phys. Chem. Solids*, **53**, 755-759 (1992).

[82] B. Bagautdinov, M. Novikova, M. Blomberg, G. Chapuis, X-ray study of phase transitions in $Cs_3Sb_2I_9$ crystal, *Solid State Commun*., **111**, 361-366 (1999).

[83] C. Zuo, L. Ding, Lead-free perovskite materials $(NH_4)_3Sb_2I_xBr_{9-x}$, *Angew. Chem.,* **56**, 6528-6532 (2017).

[84] M. Boopathi, L. Lin, G. Li, P. Wang, W. Chu, A. Singh, Solution-processable antimony-based light-absorbing materials beyond lead halide perovskites, *J. Mater. Chem. A*, **5**, 20843-20850 (2007).

[85] T. Buonassisi, L. Mariya, D. Nathan, R. Jeremy, S. Sun, A-site cation in inorganic $A_3Sb_2I_9$ perovskite influences structural dimensionality, exciton binding energy, and solar cell performance, *Chem. Mater*., **30**, 3734-3742 (2018).

[86] A. Mourtada, S. Ahmed, S. Sajid, M. Rashad, M. Ali, Copper-substituted lead perovskite materials constructed with different halides for working $(CH_3NH_3)_2CuX_4$-based perovskite solar cells from experimental and theoretical view, *ACS Appl. Mater. Interfaces*, **10**, 11699-11707 (2018).

[87] M. Bidikoudi, K. Emmanuel, Novel approaches and scalability prospects of copper based hole transporting materials for planar perovskite solar cells, *J. Mater. Chem. C*, **7**, 13680-13708 (2019).

[88] N. Wijeyasinghe, T. Leonidas, R. Anna, W. Sit, Z. Fei, T. Du, Copper (I) selenocyanate (CuSeCN) as a novel

hole-transport layer for transistors, organic solar cells, and light-emitting diodes, *Adv. Funct. Mater.*, https://doi.org/10.1002/adfm.201707319 (2018).

[89] W. Haoxin, Z. Yu, J. Xiao, J. Li, C. Bin, X. Yang, Efficient and stable inverted planar perovskite solar cells employing CuI as hole-transporting layer prepared by solid–gas transformation, *Energy Technol.*, **5**, 1836-1843 (2017).

[90] Y. Weili, F. Li, H. Wang, A. Erkki, C. Yin, L. Bin, X. Wang, Ultrathin Cu_2O as an efficient inorganic hole transporting material for perovskite solar cells, *Nanoscale*, **8**, 6173-6179 (2016).

[91] Y. ZhiKai, W. Fu, W. Liu, Z. Zhang, Y. Liu, J. Yan, Solution-processed CuO_x as an efficient hole-extraction layer for inverted planar heterojunction perovskite solar cells, *Chin. Chem. Lett.*, **28**, 13-18 (2017).

[92] B. Mansoura, M. Rawia, W. Sandra, M. Mark, R. Thierry, M. Edoardo, A new lead-free 1D hybrid copper perovskite and its structural, thermal, vibrational, optical and magnetic characterization, *J. Mater. Chem. C*, **9**, 5970-5976 (2021).

[93] C. Daniele, A. Dewi, Y. Jun, A. Bruno, C. Shi, B. Tom, Lead-free $MA_2CuCl_xBr_{4-x}$ hybrid perovskites, *Inorg. Chem.*, **55**, 1044-1052 (2016).

[94] Z. Kang, X. Hao, W. Bo, L. Jiang, B. Fan, A. Yang, Stable copper-based 2D perovskite $(NH_3C_3H_6NH_3)CuBr_4$ thin film processed from green solvent for thermoelectric application, *EcoMat*: https://doi.org/10.1002/eom2.12163 (2022).

[95] W. Cuncun, Q. Zhang, W. Luo, Y. Liu, H. Ziru, Z. Chen, H. Ting, S. Wei, S. Wang, L. Xiao, The dawn of lead-free perovskite solar cell: highly stable double perovskite $Cs_2AgBiBr_6$ film, *Adv. Sci.*, DOI: 10.1002/advs.201700759 (2018).

[96] Z. Dandan, B. Wang, C. Liang, T. Liu, Q. Wei, S. Wang, K. Wang, G. Xing, S. Peng, X. Li, Facile deposition of high-quality Cs2AgBiBr6 films for efficient double perovskite solar cells, *Sci. China Mater.*, **63**, 1518-1525 (2020).

[97] T. Maximillian, H. Rik, M. Armer, G. Ebadi, M. Mahdi, 2D/3D hybrid $Cs_2AgBiBr_6$ double perovskite solar cells: improved energy level alignment for higher contact-selectivity and large open circuit voltage, *Adv. Energy Mater.*, https://doi.org/10.1002/aenm.202103215 (2022).

[98] Y. Guan, S. Huang, X. Wu, A. Lu, H. Ding, Structural, optical, and thermal properties of $Cs_2SnI_{6-x}Br_x$ mixed perovskite solid solutions, *Eur. J. Inorg. Chem.*, https://doi.org/10.1002/ejic.201900120 (2019).

[99] F. Ping, H. Peng, Z. Zheng, Z. Chen, S. Tan, X. Chen, Single-source vapor-deposited $Cs_2AgBiBr_6$ thin films for lead-free perovskite solar cells, *Nanomaterials (Basel),* doi: 10.3390/nano9121760 (2019).

[100] N. Rodkey, S. Kaal, J. Henk, F. Palazon, A. Yorick, Pulsed laser deposition of $Cs_2AgBiBr_6$: from mechanochemically synthesized powders to dry, single-step deposition, *Chem. Mater.*, **33**, 7417-7422 (2021).

[101] I. Femi, Z. Yue, L. Liao, Y. Yang, X. Ma, Q. Wang, K. Wang, Composition stoichiometry of $Cs_2AgBiBr_6$ films for highly efficient lead-free perovskite solar cells, *Nano Lett.*, **19**, 2066-2073 (2019).

[102] X. Bo, X. Tan, Z. Yi, Y. Luo, Q. Jiang, J. Yang, Band matching strategy for all-inorganic $Cs_2AgBiBr_6$ double perovskite solar cells with high photovoltage, *ACS Appl. Materi. Interfaces*, **13**, 37027-30734 (2021).

[103] E. Greul, T. Bein, A. Binek, D. Pablo, L. Petrus, Highly stable, phase pure $Cs_2AgBiBr_6$ double perovskite thin films for optoelectronic applications, *J. Mater. Chem. A*, **5**, 19972-19981 (2017).

[104] L. Ying, A. Nag, L. Manna, Z. Xia, Lead-free double perovskite $Cs_2AgInCl_6$, *Angew. Chem.*, **133**, 11696-11707 (2021).

[105] Z. Jun, Z. Xia, S. Maxim, X. Zhang, Q. Liu, Composition design, optical gap and stability investigations of lead-free halide double perovskite $Cs_2AgInCl_6$, *J. Mater. Chem. A*, **5**, 15031-15037 (2017).

[106] N. Weihua, W. Feng, W. Bo, Z. Yan, J. Lu, Long electron–hole diffusion length in high-quality lead-free double perovskite films, *Adv. Mater.*, https://doi.org/10.1002/adma.201706246 (2018).

[107] Y. Sozen, S. Ozen, H. Sahin, Cesium manganese chloride: Stable lead-free perovskite from bulk to single layer, *J. Magn. Magn. Mater.*, https://doi.org/10.1016/j.jmmm.2021.167845 (2021).

[108] T. Shodruc, V. Anastasia, S. Leonid, V. Knotko, N. Koji, Indium doping of lead free perovskite Cs_2SnI_6, *Front. Chem.*, doi: 10.3389/fchem.2020.00564 (2020).