Review

Lead-Free Halide Double Perovskites: A Review of the Structural, Optical, and Stability Properties as Well as Their Viability to Replace Lead Halide Perovskites

Edson Meyer ¹, Dorcas Mutukwa ^{1,2,*} , Nyengerai Zingwe ^{1,2} and Raymond Taziwa ¹

¹ Fort Hare Institute of Technology, University of Fort Hare, Alice 5700, South Africa; emeyer@ufh.ac.za (E.M.); nzingwe@ufh.ac.za (N.Z.); rtaziwa@ufh.ac.za (R.T.)

² Department of Chemistry, University of Fort Hare, Alice 5700, South Africa

* Correspondence: dmutukwa@ufh.ac.za; Tel.: +27-61-686-8252

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Abstract: Perovskite solar cells employ lead halide perovskite materials as light absorbers. These perovskite materials have shown exceptional optoelectronic properties, making perovskite solar cells a fast-growing solar technology. Perovskite solar cells have achieved a record efficiency of over 20%, which has superseded the efficiency of Grätzel dye-sensitized solar cell (DSSC) technology. Even with their exceptional optical and electric properties, lead halide perovskites suffer from poor stability. They degrade when exposed to moisture, heat, and UV radiation, which has hindered their commercialization. Moreover, halide perovskite materials consist of lead, which is toxic. Thus, exposure to these materials leads to detrimental effects on human health. Halide double perovskites with $A_2B'B''X_6$ ($A = \text{Cs, MA}$; $B' = \text{Bi, Sb}$; $B'' = \text{Cu, Ag}$, and $X = \text{Cl, Br, I}$) have been investigated as potential replacements of lead halide perovskites. This work focuses on providing a detailed review of the structural, optical, and stability properties of these proposed perovskites as well as their viability to replace lead halide perovskites. The triumphs and challenges of the proposed lead-free $A_2B'B''X_6$ double perovskites are discussed here in detail.

Keywords: perovskite solar cells; halide double perovskites; light absorbers; bandgap; optoelectronic

1. Introduction

Perovskite solar cells (PSCs) constitute a new emerging low-cost solar technology that has the potential to dominate or co-exist with silicon solar technologies [1]. PSCs have sparked major interest in the photovoltaic community due to their remarkable photon conversion efficiency, which has increased from 3.8% to 22.7% [2] in less than 10 years, as compared to their predecessors, DSSCs. DSSCs have only managed to reach an efficiency of 11.9% over two decades of research. PSCs employ perovskite materials as light-harvesting materials. These perovskite materials have shown remarkable photovoltaic properties such as long charge diffusion length, direct bandgap, tunable bandgap, low carrier recombination, high carrier mobilities, high molar extinction coefficient, and strong absorption in the visible spectrum [3,4].

PSCs consist of (1) an organic-inorganic metal halide perovskite light harvester e.g., $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3), (2) a hole-transporting material (HTM), e.g., spiroMeOTAD (2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spiro-bifluorene), (3) an electron-transporting material (ETM), e.g., [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), (4) a transparent conducting electrodes, e.g., an indium tin oxide (ITO) or fluorine-doped tin oxide (FTO) electrode, (5) a back contact, e.g., Au, and (6) a mesoporous layer of TiO_2 nanoparticles for mesoscopic cells. The PSC device configurations

can be classified into mesoporous and planar heterojunction devices; further classification introduces the n-i-p and p-i-n devices as shown in Figure 1. These two configurations differ due to the placement of the ETM or HTM. When the device configuration has the HTM thin film above the perovskite layer, the architecture is an n-i-p. Conversely, a configuration with the ETM thin film above the perovskite layer is called a p-i-n architecture [5]. Mesoscopic devices usually incorporate porous TiO_2 nanoparticles or ZnO as an active scaffold material and Al_2O_3 or ZrO_2 as passive scaffolds [6].

Figure 1. Perovskite solar cell (PSC) device architectures: (a) planar n-i-p device; (b) mesoscopic n-i-p device; (c) planar p-i-n device; and (d) mesoscopic p-i-n device.

The most commonly studied perovskite materials are hybrid halide perovskites with a formula ABX_3 , where A is a monovalent cation such as methylammonium (MA^+), formamidium (FA^+); B is a divalent metal cation such as Pb^{2+} ; and X is a halide such as Cl^- , I^- , or Br^- . The structure of an ideal perovskite can be described as cubic with B atoms in the center surrounded by an octahedron of anions. The A cations are at the interstices, surrounded by eight octahedra in the cuboctahedral gap, forming a three-dimensional (3D) network [7]. Organic-inorganic hybrid perovskites such as MAPbI_3 and FAPbI_3 are the most commonly used perovskites in solar cells.

The degradation of PSCs from exposure to moisture, UV radiation, heat, and oxygen as well as toxicity concerns are some of the challenges hindering the commercialization prospects of PSCs. The use of lead in PSCs is of great concern since lead is very toxic, thus any encapsulation failures or leakages would result in detrimental effects [8]. Lead is a renowned toxic heavy metal that bio-accumulates in living organisms. It is carcinogenic, with children being more vulnerable to exposure than adults due to a high frequency of pica, as well as higher intestinal and retention rates [9,10]. Exposure to even minimal amounts of lead may result in mental retardation in children, developmental delay, fatal infant encephalopathy, congenital paralysis, acute or chronic damage to the nervous system, epileptics, or kidney, liver and gastrointestinal damage [11,12].

With the photovoltaic community aware of the dangers associated with the use of lead in PSCs [13,14], research has been focused on replacing lead in perovskite materials with other non-toxic metals such as bismuth, germanium, and antimony [15,16]. This review paper is focused on presenting the structural, optical, and stability properties of halide double perovskites and the research progress attained so far towards producing lead-free PSCs.

2. Heterovalent Substitution

Heterovalent substitution is an effective approach that has been adopted and led to significant progress in the quest to produce lead-free halide perovskites. The first approach involves replacing the Pb^{2+} cation with a trivalent cation such as Sb^{3+} or Bi^{3+} , resulting in a vacancy ordered $\text{A}_3\text{B}_2\text{X}_9$ perovskite, where A is a cation such as Cs^+ ; B is a cation such as Sb^{3+} or Bi^{3+} ; and X is a halide such as Br^- [17]. Park et al. [18] reported a power conversion efficiency (PCE) of about 1% obtained with a PSC employing a hexagonal $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite belonging to the $P6_3/mmc$ space group as a light absorber. Zhang et al. [19] replaced the Cs^+ with MA^+ to form a hybrid $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ perovskite which exhibited a PCE of 1.64% when used as a light harvester in PSCs. Unfortunately, the $\text{A}_3\text{B}_2\text{X}_9$ perovskites have been reported to exhibit low structural dimensionality, which results in large bandgaps (>2 eV) as well as poor photovoltaic performances [20]. Hence, the use of $\text{A}_3\text{B}_2\text{X}_9$ perovskites to replace lead halide perovskite light absorbers is not viable due to the issues raised above.

The second approach involves the replacement of lead with two cations, (1) a monovalent metal cation and (2) a trivalent metal cation, to give an average of +2 valence state, which the same as that of Pb^{2+} in hybrid lead halide perovskites. The halide double perovskites can be described by the formula $\text{A}_2\text{B}'\text{B}''\text{X}_6$, with A being a monovalent cation such as Cs^+ or MA^+ , B' being a trivalent metal cation such as Bi^{3+} or Sb^{3+} , B'' being a monovalent metal such as Cu^+ , Ag^+ , or Na^+ ; and X being a halide such as Cl^- , Br^- , or I^- [21]. Most of the investigated halide double perovskites have Sb^{3+} and Bi^{3+} as the replacement for Pb^{2+} [20,22,23]. Bi^{3+} and Pb^{2+} are isoelectronic while Sb^{3+} is isoelectronic with Sn^{2+} which is another ideal ion to replace Pb^{2+} . Therefore, replacing Pb^{2+} with Sb^{3+} and Bi^{3+} would be ideal as it is believed that the excellent optoelectronic properties of hybrid lead halide perovskites are due to the electronic configuration of Pb^{2+} ($6s^2p^0$) [24,25].

Two empirical quantities, the Goldschmidt tolerance factor (t) and the octahedral factor (μ), can be used to predict the crystallographic stability of $\text{A}_2\text{B}'\text{B}''\text{X}_6$ perovskites. The formation of halide perovskites generally occurs with a Goldschmidt tolerance factor range of $0.81 \leq t \leq 1.0$ and an octahedral factor range of $0.44 \leq \mu \leq 0.9$ [26]. The t_{eff} and μ_{eff} can be defined as given in Equations (1) and (2), respectively.

$$t_{\text{eff}} = (R_A + R_X) / \sqrt{2[(R_{B'} + R_{B''})/2 + R_X]} \quad (1)$$

$$\mu_{\text{eff}} = (R_{B'} + R_{B''}) / 2R_X \quad (2)$$

Here, R_A , R_B , $R_{B''}$, and R_X are the Shannon ionic radii of A, B' , B'' , and X, respectively [27]. When t or μ lies within the range, it does not necessarily mean that the required perovskite will form or that the perovskite is stable [28]. These two empirical quantities have been used for the screening and discovery of new halide perovskites. Besides Sb and Bi, other trivalent cations can be investigated as potential replacements of Pb^{2+} such as lanthanides, which are thought to have interesting optoelectronic properties [29]. Lanthanide-based halide double perovskites have been synthesized before [30], although to date there has been no report on their optoelectronic and photovoltaic properties. Volonakis et al. [31] stated that obtaining density function theory (DFT) predictions of the optoelectronic properties of transition metals, actinides, and lanthanide double perovskites is challenging. Perhaps the optoelectronic and photovoltaic properties of these lanthanide-based halide double perovskites can be assessed from experimental analysis rather than from theoretical calculations.

Noble metals Cu^+ , Ag^+ , and Au^+ are normally used as the B'' monovalent cation since they possess good optoelectronic properties. Na^+ (116 pm) can also be used as a B'' monovalent because its crystal radius is comparable to that of Ag^+ (129 pm) [32]. Compared to Cu and Ag, Au is expensive, making it unsustainable for use in these perovskites. Theoretical calculations for $\text{A}_2\text{B}'\text{InX}_6$ ($\text{A} = \text{Rb}$, Cs ; $\text{B}' = \text{Ag}$, Cu , and $\text{X} = \text{Cl}$, Br) bandgaps yielded direct bandgaps in the range of 1.36–1.50 eV [33]. Although these bandgaps are close to the optimal bandgap of 1.34 eV for application in single junction solar cells, the synthesis of the copper-based double perovskite is not viable because Cu crystallizes in a CuX_4 coordinate instead of a CuX_6 coordinate, which is present in double perovskites as discussed

below. In^+ can also be used as a B' cation; however, it quickly oxidizes to In^{3+} , thereby disrupting the perovskite structure. The next section gives a detailed literature review on the structure of $\text{A}_2\text{B}'\text{B}''\text{X}_6$ double perovskites.

3. Structure

The most investigated halide double perovskites have been reported to possess a cubic face-centered structure belonging to the space group $Fm-3m$ and with a lattice parameter ranging from approximately 10–12 Å [34–36]. The structure is similar to the ABX_3 perovskite structure, composed of a 3D network of corner connected octahedra, with Cs^+ ions in the center of the cuboctahedron interstices. Unlike the hybrid halide perovskites where the perovskite structure is obtained by just B^{2+} centered octahedron [7], the halide double perovskite structure is built of alternating B' and B'' centered octahedrons of $\text{B}'\text{X}_6$ and $\text{B}''\text{X}_6$ in a 3D framework known as rock salt ordering. The conventional ideal structures of the hybrid halide perovskites and halide double perovskites are given below in Figure 2. The structure of halide double perovskites is similar to that of oxide double perovskites such as $\text{Sr}_2\text{FeMoO}_6$, which are known to possess interesting properties such as ferroelectricity, ferromagnetism, and superconductivity [37].

Figure 2. (a) Structure of ideal ABX_3 halide perovskites. (b) Structure of ideal $\text{A}_2\text{B}'\text{B}''\text{X}_6$ halide double perovskites. Reproduced with permission from Reference [21]. Elsevier, 2018.

Wei et al. [38] synthesized a hybrid double perovskite $(\text{MA})_2\text{KBiCl}_6$ which crystallized in a 3D distorted structure belonging to the $R3-m$ space group, as shown in Figure 3, with lattice parameters of $a = 7.84$ Å and $c = 20.99$ Å. The distortion of the $(\text{MA})_2\text{KBiCl}_6$ structure from the cubic structure which is exhibited by most halide double perovskites is due to the differences in size between the K^+ and Bi^{3+} ionic radii. The Bi–Cl bond length (2.68 Å) was shorter than that of K–Cl (3.05 Å). The MA^+ alternate along the c direction with the symmetry equivalent MA^+ adopting opposite orientations and C–N bond lengths of 1.35 Å. The bond length of N–Cl is 3.41 Å, which is shorter than the C–Cl bond length of 3.85 Å; this implies hydrogen bonding. The degree of tilting in the distorted structure is less than in the orthorhombic phase of the MAPbCl_3 hybrid perovskite. The experimental X-ray diffraction (XRD) studies were in agreement with the DFT (density function theory) geometry optimization in $R3-m$ results with lattice parameters of $a = 7.82$ Å and $c = 20.99$ Å. $(\text{MA})_2\text{KBiCl}_6$ exhibited a wide and indirect bandgap (3.0 eV) similar to the bandgap of MAPbCl_3 , rendering it unsuitable for single junction solar cell application.

Figure 3. Crystal structure of $(\text{MA})_2\text{KBiCl}_6$, obtained from single crystal X-ray diffraction, viewed along (a) the c axis, (b) the a axis, and (c) tilted to show the MA location. Red: Bi, brown: K, green: Cl, white: C, blue: N. BiCl_6 and KCl_6 octahedra are shown in blue and purple, respectively. Reproduced with permission from Reference [38]. Royal Society of Chemistry, 2016.

However, Wei et al. [39] also reported another hybrid double perovskite $(\text{MA})_2\text{AgBiBr}_6$ that crystallized into an ordered 3D cubic structure belonging to the space group $Fm-3m$ and with a lattice parameter of 11.64 Å. Surprisingly, the MA^+ orientation was disordered in the cavity, as observed in the $(\text{MA})_2\text{KBiCl}_6$ double perovskite. The Ag–Br bond length was 2.95 Å, while that of Bi–Br was 2.87 Å. To the best of our knowledge, the photovoltaic performance of the reported $(\text{MA})_2\text{AgBiBr}_6$ double perovskite has not been reported. This might be due to its wide bandgap, which makes it unsuitable to replace hybrid lead halide perovskites.

Moreover, Deng et al. [40] reported a $(\text{MA})_2\text{TlBiBr}_6$ that is isoelectronic with MAPbBr_3 and that also crystallized into a 3D cubic structure belonging to the space group $Fm-3m$ with a lattice parameter of 11.76 Å. The $(\text{MA})_2\text{TlBiBr}_6$ double perovskite had a direct bandgap of 2.16 eV. However, thallium is more toxic than lead [41], thus rendering $(\text{MA})_2\text{TlBiBr}_6$ unsuitable to replace hybrid halide perovskites. Volonakis et al. [31] synthesized another lead-free double perovskite of the formula $\text{Cs}_2\text{InAgCl}_6$. The density functional theory/local density approximation (DFT/LDA) calculations predicted that this lead-free perovskite $\text{Cs}_2\text{InAgCl}_6$ would crystallize into an ordered cubic structure. Experimental findings by Volonakis et al. were in close agreement with the DFT/LDA approximation, which reported the presence of a 3D cubic structure belonging to the space group $Fm-3m$ and with a lattice parameter of 10.47 Å. This was further cemented by the XRD analysis shown here in Figure 4. Even though the $\text{Cs}_2\text{InAgCl}_6$ double perovskite crystallized into a 3D structure, it exhibited a direct wide bandgap of 3.3 eV, which makes it unsuitable for single junction solar cell application.

Hybrid lead halide perovskites have shown remarkable photovoltaic performance when used in PSCs. Various structural dimensions, such as two-dimensional (2D) and 3D, of these hybrid lead halide perovskites have been explored as light absorbers in PSCs. The 3D structures of these perovskites have shown a better photovoltaic performance, which is ideal for single junction solar cell applications [42,43]. Most studied halide double perovskites exhibited 3D structures; however, their bandgaps were very wide, which means that the photovoltaic performance of these perovskites is not only dependent on structural dimensionality. Xiao et al. [43] introduced the concept of electronic dimensionality to help explain why the 3D halide double perovskites do not exhibit ideal photovoltaic performance as their 3D hybrid halide perovskites counterparts do. Electronic dimensionality is the connectivity of lower conduction band and upper valence band atomic orbitals. High electronic dimensionality is needed for perovskites to exhibit good photovoltaic performance. Even though the halide double perovskites crystallize into 3D structural dimension, they might exhibit low electronic dimensionality, rendering them unsuitable for single junction solar cell application.

Figure 4. Measured powder XRD pattern for $\text{Cs}_2\text{InAgCl}_6$ (**top**), and the XRD pattern calculated from the atomistic model optimized using density functional theory/local density approximation (DFT/LDA) (**bottom**). Reproduced with permission from Reference [31]. American Chemical Society, 2017.

4. Optical

Optical properties of halide double perovskites are determined by investigating their visible light-harvesting capacity. This is normally done through the calculation of absorption coefficients as well as the determination of their energy bandgaps. Since the absorption threshold is inversely proportional to the energy bandgap, perovskites with higher bandgaps should have narrow absorption in the visible range. Lead-free halide double perovskites exhibit both direct and indirect bandgaps. UV-Vis diffuse spectra recorded by McClure et al. [36] showed that both $\text{Cs}_2\text{AgBiCl}_6$ and $\text{Cs}_2\text{AgBiBr}_6$ exhibited indirect bandgaps. The calculation of optical bandgaps for the synthesized perovskites using the Kubelka-Munk equation yielded bandgaps of 2.19 eV and 2.77 eV for $\text{Cs}_2\text{AgBiCl}_6$ and $\text{Cs}_2\text{AgBiBr}_6$, respectively. Bandgaps for the hybrid lead perovskites were 2.26 eV and 3 eV for MAPbBr_3 and MAPbCl_3 respectively. In this work, it was noted that despite observable similarities between the $\text{Cs}_2\text{AgBiX}_6$ perovskites and the MAPbX_3 , mild absorption onset was observed in the double perovskites as compared to MAPbBr_3 and MAPbCl_3 . This is clearly illustrated in Figure 5.

The late absorption onset was attributed to the indirect bandgap in double perovskites. The indirect bandgaps of $\text{Cs}_2\text{AgBiX}_6$ perovskites are not ideal for thin film photovoltaic applications; however, recent developments have shown that bandgaps can be transformed from indirect to direct. Since bandgaps are dependent on the lattice parameters of the developed perovskites they can therefore be manipulated from indirect to direct by varying operational temperature, pressure, and doping with another element.

Other researchers have nonetheless fabricated halide double perovskites with direct bandgaps. Volonakis and associates [31] synthesized $\text{Cs}_2\text{InAgCl}_6$ with a direct bandgap of 3.3 eV. The onset of absorption for this perovskite was observed at 380 nm with a second absorption at 585 nm. Comparison of the optical absorption spectra for $\text{Cs}_2\text{InAgCl}_6$ and $\text{Cs}_2\text{InAgBr}_6$ with those of Si, GaAs, and MAPbI_3 shows that despite having a direct bandgap, the absorption coefficient for $\text{Cs}_2\text{InAgCl}_6$ is much smaller than those of the other perovskites throughout the visible spectrum. A comparable absorption coefficient for halide double perovskites can only be obtained if the synthesis of an ideal crystal of $\text{Cs}_2\text{InAgBr}_6$ was successful. Investigation into the optical characteristics of the sodium-based

perovskites Cs_2NaBX_6 (where $B = \text{Sb, Bi}$; $X = \text{Cl, Br, I}$) yielded iodide perovskites $\text{Cs}_2\text{NaSbI}_6$ and $\text{Cs}_2\text{NaBiI}_6$, with optimal bandgaps of 2.03 eV and 2.43 eV, respectively. Thus, they can potentially be used in solar cell applications. As illustrated in Figure 6, $\text{Cs}_2\text{NaSbI}_6$, $\text{Cs}_2\text{NaBiI}_6$, and $\text{Cs}_2\text{NaSbBr}_6$ exhibited efficient absorption coefficients in the visible range. This was attributed to the fact that transitions in these compounds are p-p valence to conduction band transitions [44]. To date, bandgaps of all synthesized double halide perovskites are still too large for single junction solar cell application.

Figure 5. (a) UV-Vis diffuse reflectance spectra for $\text{Cs}_2\text{AgBiBr}_6$ and MAPbBr_3 , (b) UV-Vis diffuse reflectance spectra for $\text{Cs}_2\text{AgBiCl}_6$ and MAPbBr_3 . Reproduced with permission from Reference [36]. American Chemical Society, 2016.

Figure 6. Optical absorption spectra for the Cs_2NaBX_6 double perovskites ($B = \text{Bi, Sb}$; $X = \text{Cl, Br, I}$). Reproduced with permission from Reference [44]. Elsevier, 2018.

Another class of halide double perovskite which could possess bandgaps that are useful for photovoltaic applications is the class of hybrid halide double perovskites. Even though organic compounds are known to be susceptible to thermal instability, hybrid halide double perovskites have otherwise shown excellent thermal stability. Wei et al. [39] fabricated one such hybrid perovskite, $(\text{MA})_2\text{AgBiBr}_6$, which possessed a smaller bandgap whilst being thermally stable up to 400 °C. Optical bandgaps from absorption and diffuse reflectance spectra yielded an indirect bandgap of 2.02 eV, which is comparable to its cesium-based analogue reported by Volonakis et al. [34]. Wei and co-workers reported that the bandgap of $(\text{MA})_2\text{AgBiBr}_6$ is narrow enough to exhibit semiconducting properties; however, its electronic conductivity is deemed to be lower than its ionic conductivity at $4.8 \times 10^8 \Omega \cdot \text{cm}$.

Due to the wide indirect bandgap of $(\text{MA})_2\text{AgBiBr}_6$, a low PCE should be expected. The wide bandgaps minimize the potential for any photovoltaic application. In a similar manner, Wei et al. [38] also synthesized $(\text{MA})_2\text{KBiBr}_6$, which was reported to have similarities to MAPbCl_3 . UV-Vis measurements obtained two values of 3.04 and 3.37 eV as the optical bandgaps. The theoretical band structure of $(\text{MA})_2\text{KBiBr}_6$ using DFT recognized an indirect bandgap of 3.08 eV, which is consistent with the experimental data. In this work, Wei and colleagues revealed that the main contributors to the electronic density of states near the bandgap edge were Bi and Cl. The valence band was composed of Bi-6s and Cl-3p antibonding, whereas the conduction band was composed of Bi-6p, Cl-3p, and Cl-3s. The optical bandgaps for both hybrid halide double perovskites are unsuitable for single junction solar cell application.

5. Stability

5.1. Influence of Light and Moisture on Stability

The most significant drawback associated with perovskite materials and solar cells has been their poor stability when exposed to heat, oxygen, humidity, and illumination [45]. The best-performing hybrid lead halide perovskite, MAPbI_3 , undergoes severe degradation when exposed to weather elements. It has been reported that MAPbI_3 changes phase at the onset of degradation, culminating in accelerated decomposition to PbI_2 [46]. In comparison, halide double perovskites have shown remarkable stability in various weather elements such that they might be the answer to the stability issues in perovskite solar cells.

McClure et al. [36] probed the stability of $\text{Cs}_2\text{AgBiCl}_6$ and $\text{Cs}_2\text{AgBiBr}_6$ in ambient atmosphere. When the samples were placed in darkness for a period of two weeks, no changes were observed on the exposed surfaces. However, darkening was observed when the samples were exposed to visible light. Subsequent reflectance measurements proved that the degradation of the halide double perovskite occurred, as shown in Figures 7 and 8 below.

Figure 7. UV-Vis diffuse reflectance spectra showing the light stability of CsAgBiCl_6 after two and four weeks of light exposure. Reproduced with permission from Reference [36]. American Chemical Society, 2016.

As clearly indicated in Figure 7, $\text{Cs}_2\text{AgBiCl}_6$ undergoes minimum degradation during a month's exposure to light, which is reflected by a minimal decrease in total reflectance. In contrast, $\text{Cs}_2\text{AgBiBr}_6$ undergoes severe degradation characterized by a sharp decline in total reflectance, as shown in Figure 8.

Figure 8. UV-Vis diffuse reflectance spectra showing the light stability of CsAgBiBr_6 after two and four weeks of light exposure. Reproduced with permission from Reference [36]. American Chemical Society, 2016.

The instability of bromine-based double perovskites was also observed by Volonakis et al. [31]. Their synthesis of double halide $\text{Cs}_2\text{InAgX}_6$ yielded a stable $\text{Cs}_2\text{InAgCl}_6$ with no observable structural decomposition when exposed to ambient conditions for more than three months. The fabrication of the bromide perovskite was, however, not successful at all. This anomaly was attributed to the fact that the In^{3+} radii is too small to properly coordinate 6Br^- anions. A pre-synthesis assessment of $\text{Cs}_2\text{AgBiBr}_6$ stability using the Goldschmidt empirical criteria yields tolerance and octahedral factors of $t = 0.83$ and $\mu = 0.584$, respectively. This indicates that a structurally stable $\text{Cs}_2\text{AgBiBr}_6$ can be feasibly fabricated. Comparison of the radii between Bi^{3+} and the Br^- suggests that the bismuth cation is capable of adequately coordinating six bromine anions. Therefore, more research work is required to determine why $\text{Cs}_2\text{AgBiBr}_6$ is unstable. Consequently, at the present moment effective protection against the effects of light can only be minimized by encapsulation.

5.2. Influence of Temperature on Stability

Solar panels require thermal stability since they function under elevated temperatures. As per the international standard, panels must withstand temperatures reaching up to 85°C , corresponding to 0.093 eV. Hence, in order to withstand these temperatures, the energy of formation for lead-free double halide perovskites must be higher than 0.093 eV. Pre-synthesis assessment of the thermodynamic stability of halide double perovskites is done through the calculation of the energies of formation based on Equation (3).

where $\Delta H = 2H(\text{Cs}_2\text{B}'\text{B}''\text{X}_6) - H(\text{Cs}_2\text{B}'\text{X}_9) + 2H(\text{B}''\text{X}) + H(\text{CsX})$.

Table 1 depicts the calculated formation energies for some common double halide perovskites. A negative enthalpy of formation indicates that the perovskite is presumed to be thermodynamically stable, whereas a positive ΔH implies that the perovskite is spontaneous and unstable. From Table 1, it is clear that the sodium-based chlorides as well as $\text{Cs}_2\text{AgBiI}_6$ have an endothermic phase decomposition; thus, they can be deemed to be thermodynamically stable. In order to understand the effects of temperature on the double halide perovskites, an experimental analysis was conducted in which the synthesized perovskites were exerted to a wide range of temperatures. One such study on the thermal stability of $\text{Cs}_2\text{AgBiBr}_6$ was conducted by Dong et al. [23]. Results from his work showed that $\text{Cs}_2\text{AgBiBr}_6$ undergoes minimal thermal expansion as compared to other perovskites. Since the thermal stability of the perovskite depends on the crystal structure and bond strength, measurements

on the expansion of the unit cell were taken. For the temperature range from 120 to 360 °C, the cell volume and axis length increased by 0.67% and 2.01%, respectively.

Table 1. Calculated values of enthalpy of formation for various double halide perovskites.

Compounds	$\Delta H/\text{eV}$	Reference
$\text{Cs}_2\text{AgBiCl}_6$	+0.57	[47]
$\text{Cs}_2\text{AgBiBr}_6$	+0.38	[47]
$\text{Cs}_2\text{AgBiI}_6$	−0.41	[47]
$\text{Cs}_2\text{InBiCl}_6$	+0.01	[47]
$\text{Cs}_2\text{InBiBr}_6$	−0.04	[47]
$\text{Cs}_2\text{NaSbCl}_6$	−0.19	[44]
$\text{Cs}_2\text{NaBiCl}_6$	−0.43	[44]
$\text{Cs}_2\text{NaSbI}_6$	+0.49	[44]
$\text{Cs}_2\text{NaBiI}_6$	+0.40	[44]
$\text{Cs}_2\text{NaBiBr}_6$	+0.01	[44]
$\text{Cs}_2\text{NaSbBr}_6$	+0.11	[44]

In comparison to other perovskite compounds, the stability of $\text{Cs}_2\text{AgBiBr}_6$ (shown in Table 2) was attributed to the stronger bonding characteristics and the absence of organic components which impact higher structural stiffness, thus resulting in a low susceptibility to temperature perturbation. Perhaps the most significant development for lead-free halide double perovskites has been the discovery that cesium-based perovskites withstand temperatures up to 300 °C. To the best of our knowledge, no analysis has been performed on halide double perovskites, but results obtained from the investigation of CsPbI_3 showed that cesium could be the answer to attaining perovskite stability [48]. This fact bodes well for most halide double perovskites since they contain cesium. Niu et al. [49] produced thermally stable $\text{Cs}_x\text{MA}_{1-x}\text{PbI}_3$ perovskites compared to the best-performing MAPbI_3 . An analysis of the results from this work showed that these perovskites were only stable for amounts of cesium between 0.09 and 0.20. Any further increase in cesium resulted in a rapid decrease of the thermal stability of the synthesized element. The addition of cesium invigorates the film deposition rate, leading to a decrease in grain size.

Table 2. Experimental values of bulk moduli B, hardness H, Young's moduli E, and linear thermal expansion coefficient α for four perovskites.

Perovskite	B(GPa)	H(GPa)	E(GPa)	$\alpha \text{ MK}^{-1}$	Reference
$\text{Cs}_2\text{AgBiBr}_6$	27.3	0.67	22.6	27.8	[23]
CsPbBr_3	15.5	0.34	15.8	37.7	[23]
MAPbI_3	10.2	0.42	10.4	43.3	[39]
$(\text{MA})_2\text{AgBiBr}_6$	7.7	0.55	7.9	44	[39]

Theoretically, plenty of halide double perovskites can be synthesized. However, their weak stability has meant that only a few have been synthesized thus far. In order to produce more stable halide double perovskites, a pre-synthesis assessment of suitable compositions, the properties of the materials to be used, and the limitations to the synthesis procedures should be known. One viable way of determining which compositions of halide double perovskites could be more stable is a strategy where a combination of first principles DFT calculations and machine learning is used to screen for stable perovskite compositions. The machine learning part is used to predict decomposition energies ΔH_D , which then provides insight and guidance on experimental studies.

Another challenge that is encountered during the fabrication of halide double perovskites is the instability associated with the starting materials. Halide double perovskites can be synthesized via various techniques such as solvent evaporation, the hydrothermal method, solid state sintering, and growth from melt. Chlorides form relatively easily, whereas bromides and iodides are very

difficult to fabricate. To date, only three iodine-based halide double perovskites have been successfully synthesized via growth from a melt. Synthesis is however reported to be more difficult for hybrid halide double perovskites due to the low decomposition temperatures of the organic starting material. As a result, synthesis techniques involving elevated temperatures have to be avoided, thereby limiting viable synthesis options. Wei et al. [38] synthesized $(\text{MA})_2\text{KBiCl}_6$ via the hydrothermal method while Li et al. [50] synthesized $(\text{MA})_2\text{AgSbI}_6$ via the solid state method in sealed vacuum tube. According to Volokanis et al. [34], the successful synthesis of $\text{Cs}_2\text{BiAgCl}_6$ can be attributed to the close match in radii between Na^+ (1.02 Å) and Ag (1.15 Å). In their work, they replaced the NaCl precursor with AgCl in the preparation of $\text{Cs}_2\text{BiNaCl}_6$. Hence, it is of particular importance that the most ideal method of synthesis be used to increase the probability of successfully fabricating a particular perovskite compound.

6. Current Progress of Halide Double Perovskites

Owing to the difficulties in the formation of high-quality and uniform halide double perovskites and thin films, the testing of the performance of halide double perovskites in photovoltaics has not been extensively reported. To date, only one halide double perovskite has been employed in a planar heterojunction solar cell. Wu et al. [51] reported a PCE of 1.44% using an Au/P3HT/ $\text{Cs}_2\text{AgBiBr}_6$ /SnO₂/ITO device architecture. The device was fabricated using low-pressure assisted solution processing which involved spin coating, pumping of low pressure, and then thermal annealing under ambient conditions. This process has also been used in the fabrication of some hybrid lead halide-based PSCs. Ning et al. [52] also fabricated a planar heterojunction solar cell that employed $\text{Cs}_2\text{AgBiBr}_6$ as a light absorber. Instead of using P3HT and SnO₂ as the HTM and ETM, respectively, Ning and co-workers employed SpiroMeOTAD and TiO₂ as the HTM and ETM, respectively. A PCE of 1% was reached by an Au/SpiroMeOTAD/ $\text{Cs}_2\text{AgBiBr}_6$ /TiO₂/ITO device architecture. Both device architectures suffered from low efficiencies, which were attributed to the poor charge injection from the light absorber to both HTMs and ETMs. However, they both showed better stability than the hybrid lead halide perovskites. The charge injection issue can be solved by changing the ETM with a more suitable one. It was found that interface modification through passivation or the deposition of polymer on the inorganic ETM improves charge extraction [53]. Therefore, using a modified ETM may help improve the charge injection of these $\text{Cs}_2\text{AgBiBr}_6$ -based heterojunction solar cells. There is also need for device optimization and bandgap engineering to change the indirect bandgap. Moreover, doping with Sb or Tl can reduce the bandgap of the $\text{Cs}_2\text{AgBiBr}_6$ double perovskite for improved efficiencies.

As outlined earlier, recent research has shown that doping these halide double perovskites could alter the type of bandgap produced as well as narrow its width. Slavney et al. [54] reported a Tl-doped $\text{Cs}_2(\text{Ag}_{1-x}\text{Bi}_{1-x})\text{Tl}_x\text{Br}_6$ double perovskite with a bandgap reduced by 0.5 eV at $x = 0.075$. However, with thallium being more toxic than lead, it might not be an ideal alternative for doping purposes. Using $\text{Cs}_2\text{AgBiBr}_6$ as a host, Du et al. [55] investigated band modification with Sb^{3+} and In^{3+} on the Bi^{3+} lattice site. Their work revealed that lattice constants of $\text{Cs}_2\text{Ag}(\text{Bi}_{1-x}\text{M}_x)\text{Br}_6$ (where M = Sb, In) decrease linearly as x increases, with In being able to replace 75% of Bi while Sb could only replace 37.5% of Bi. UV-Vis data from this work showed that the bandgap of $\text{Cs}_2\text{Ag}(\text{Bi}_{1-x}\text{In}_x)\text{Br}_6$ increased from 2.12 to 2.27 eV as x increased to 0.75. However, a decrease of 0.26 eV was noted for $\text{Cs}_2\text{Ag}(\text{Bi}_{1-x}\text{Sb}_x)\text{Br}_6$ as x increased from 0 to 0.375. The introduction of In led to the downward shifting of the conduction band minimum (CBM) as well as a downward movement of the valence band maximum (VBM) due to the reduction of Bi atoms. Therefore, in order for the bandgap to increase, the downward motion of the VBM should be greater than the downward motion of the CBM. The bandgaps of the doped perovskites remained indirect, which is still a challenge to be solved. Figure 9 shows a schematic of the energy levels of $\text{Cs}_2\text{AgBiBr}_6$ and Sb-doped $\text{Cs}_2\text{AgBiBr}_6$ halide double perovskites with various ETMs and HTMs.

Figure 9. Schematic of the energy levels of two halide double perovskites with various ETMs and HTMs [51,55–57].

In addition to photovoltaic applications, halide double perovskites have been explored for photocatalytic applications. Recently, Zhou et al. [58] reported for the first time highly crystalline $\text{Cs}_2\text{AgBiBr}_6$ nanocrystals fabricated using a hot injection method. The $\text{Cs}_2\text{AgBiBr}_6$ nanocrystals exhibited impressive photoconversion of CO_2 into solar fuels, with an electron consumption of $105 \mu\text{mol g}^{-1}$ in 6 h. Most of the experimental studies on halide double perovskites have been based on the bulk synthesis of halide double perovskites. Research efforts can also be directed towards the fabrication other halide double perovskite nanocrystals. Volonakis et al. [59] investigated the photocatalytic capabilities of $\text{Cs}_2\text{AgBiBr}_6$, $\text{Cs}_2\text{AgBiCl}_6$, $\text{Cs}_2\text{AgSbBr}_6$, and $\text{Cs}_2\text{AgInCl}_6$ in water splitting. This discovery proves that the application of halide double perovskites can go beyond replacing hybrid lead halide in PSCs. Further efforts can be dedicated to screening more halide double perovskites for photocatalytic and optoelectronic applications. Table 3 gives a summary of some of the halide double perovskites that have been studied to date.

Table 3. Summary of some of the studied halide double perovskites showing space group, synthesis techniques, and bandgaps.

Perovskite	Space Group	Synthesis Route	Bandgap (Measured/Theoretical eV)	PCE%	References
$\text{Cs}_2\text{AgInCl}_6$	<i>Fm3m</i>	Solvent evaporation	3.3/2.7 ± 0.6	-	[31]
	<i>Fm3m</i>	Hydrothermal	3.23/3.33	-	[60]
$\text{Cs}_2\text{AgBiCl}_6$	<i>Fm3m</i>	Solvent evaporation	2.77/2.62	-	[36]
	<i>Fm3m</i>	Solid state	2.2/2.4	-	[34]
	<i>Fm3m</i>	Solid state/solvent evaporation	2.4/-	-	[61]
$^1\text{Cs}_2\text{AgBiBr}_6$	<i>Fm3m</i>	Solvent evaporation	2.19/2.06	-	[36]
	<i>Fm3m</i>	Solid state	1.9/1.8	-	[34]
	<i>Fm3m</i>	Solid cooling	1.95/-	-	[35]
	<i>Fm3m</i>	Solid state/solvent evaporation	1.8/-	-	[61]
	<i>Fm3m</i>	Hydrothermal	2.05/-	1.22	[51]
	<i>Fm3m</i>	Hydrothermal	-	1.44	[52]

Table 3. Cont.

Perovskite	Space Group	Synthesis Route	Bandgap (Measured/Theoretical eV)	PCE%	References
Cs ₂ AgBiI ₆	<i>Fm3m</i>	-	-/1.6	-	[34]
Cs ₂ AuBiCl ₆	<i>Fm3m</i>	-	-/1.6	-	[34]
Cs ₂ AuBiBr ₆	<i>Fm3m</i>	-	-/1.1	-	[34]
Cs ₂ AuBiI ₆	<i>Fm3m</i>	-	-/0.5	-	[34]
Cs ₂ CuBiCl ₆	<i>Fm3m</i>	-	-/2.0	-	[34]
Cs ₂ CuBiBr ₆	<i>Fm3m</i>	-	-/1.9	-	[34]
Cs ₂ CuBiI ₆	<i>Fm3m</i>	-	-/1.3	-	[34]
Cs ₂ AgInBr ₆	<i>Fm3m</i>	-	-/1.50	-	[33]
Rb ₂ AgInCl ₆	<i>Fm3m</i>	-	-/2.5	-	[33]
Rb ₂ AgInBr ₆	<i>Fm3m</i>	-	-/1.46	-	[33]
Rb ₂ CuInCl ₆	<i>Fm3m</i>	-	-/1.36	-	[33]
Rb ₂ CuInBr ₆	<i>Fm3m</i>	-	-/0.63	-	[33]
Cs ₂ Au ^I Au ^{III} Cl ₆	<i>I4/mmm</i>	Solid state	2.04/-	-	[62,63]
Cs ₂ Au ^I Au ^{III} Br ₆	<i>I4/mmm</i>	Solid state	1.31/-	-	[63–65]
Cs ₂ Au ^I Au ^{III} I ₆	<i>I4/mmm</i>	Solid state	1.60/-	-	[63,64]
(MA) ₂ AgBiBr ₆	<i>Fm3m</i>	Hydrothermal	2.0/2.02	-	[39]
(MA) ₂ KBiCl ₆	<i>R3m</i>	Hydrothermal	3.04/3.08	-	[38]
(MA) ₂ AgSbI ₆	<i>R3m</i>	Solid state	1.93/2.12	-	[50]

¹ Has been tested in a planar heterojunction solar cell.

7. Conclusions

This review focused on the structural, stability, and optical properties of halide double perovskites. Most of the studied double perovskites crystallized into 3D structures and exhibited better stability than hybrid lead halide perovskites. This may be attributed to the replacement of organic cations (FA⁺, MA⁺) with an inorganic cation, Cs⁺. However, the present levels of stability in PSCs still require encapsulation to prevent degradation; thus, more research is needed to produce truly effective and stable halide double perovskites. Most of the reported halide double perovskites have exhibited indirect and wide bandgaps, which are not suitable for solar photovoltaic applications. A few of the halide double perovskites such as Cs₂InAgCl₆ have direct bandgaps and can be employed in tandem solar cells since they have wide bandgaps. Perhaps investigating other trivalent cations such as lanthanide 3⁺ cations would produce more promising results. To the best of our knowledge, only the Cs₂AgBiBr₆ halide double perovskite has been employed as a light absorber in planar heterojunction solar cells, exhibiting PCE of about 1%. Considering that most halide double perovskites have wide bandgaps, investigating the performance of these halide double perovskites in tandem solar cells might produce promising results. They can also be explored in photocatalytic application. However, presently halide double perovskites might not be adequate replacements for hybrid lead halide perovskites in single junction solar cells.

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