Recent Advancements in Nontoxic Halide Perovskites: Beyond Divalent Composition Space

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ABSTRACT: Since the inception of organic–inorganic hybrid perovskites of ABX₃ stoichiometry in 2009, there has been enormous progress in envisaging efficient solar cell materials throughout the world, from both the theoretical and experimental perspectives. Despite achieving 25.5% efficiency, hybrid halide perovskites are still facing two main challenges: toxicity due to the presence of lead and device stability. Two particular families with AₓBₓXₙ and AₓMₓM’ₓXₙ stoichiometries have emerged to address these two prime concerns, which have restrained the advancement of solar energy harvesting. Several investigations, both experimental and theoretical, are being conducted to explore the holy-grail materials, which could be optimum for not only efficient but also stable and nontoxic photovoltaics technology. However, the trade-off among stability, efficiency, and toxicity in such solar energy materials is yet to be completely resolved, which requires a systematic overview of AₓBₓXₙ- and AₓMₓM’ₓXₙ-based solar cell materials. Therefore, in this timely and relevant perspective, we have focused on these two particular promising families of perovskite materials. We have portrayed a roadmap projecting the recent advancements from both theoretical and experimental perspectives for these two exciting and promising solar energy material families while amalgamating our critical viewpoint with a future outlook.

1. INTRODUCTION

The development of a nation implicitly depends on energy production, energy management, and its wise utilization. Most countries nowadays rely on conventional sources of energy, which are going to end very soon and will lead to energy crisis. Energy crisis is a combined effect of overconsumption, overpopulation, poor management, and lack of awareness. Overcoming the energy crisis is the biggest challenge before the scientific community. Focused research on nonconventional, sustainable, and most importantly renewable energy sources is needed to address the current energy scenario. Solar energy is the most promising candidate among all of the emerging renewable energy sources. Solar energy certainly has many advantages over other forms of sustainable sources like easy harvesting, relatively cleaner, low maintenance, and cost-effective. Solar cell technology has significantly evolved over the past few decades, including silicon-based solar cells, Si–Ge thin-film solar cells, dye-sensitized solar cells, and quantum dot sensitized solar cells. Nowadays, perovskite-based solar cells (PSCs) are trending worldwide and inspiring research communities all across the globe. They have appreciable properties like low fabrication cost, high photoconversion efficiency, wide tunable band gap, high absorption coefficient, long charge carrier diffusion length, high charge carrier mobility, high open-circuit voltage, etc. The perovskite structure has the stoichiometry ABX₃, where A is the organic or inorganic ligand, B is the metal cation, and X is the halogen element. Perovskites are highly versatile. They have many optoelectronic applications, namely, photodetectors, X-ray detectors, photocatalysts, light-emitting diodes (LEDs), and solar cells. The power conversion efficiency of perovskite materials increased significantly to 25.5% in 2020. In spite of the high conversion efficiency, PSCs have stability issues when exposed to ambient atmospheric conditions. Perovskites have a shorter lifetime as compared to silicon cells because they collapse easily. Instability in the structure arises due to the presence of oxygen and moisture in the atmosphere. Here, the water molecule gets trapped in the perovskite and acts as a catalyst for structure degradation. Perovskites are also highly sensitive to elevated temperatures; as the temperature increases above 100 °C, degradation occurs. A stable perovskite should be able to withstand temperatures above 85 °C. The optoelectronic performance of the device is greatly influenced by other parameters apart from temperature, moisture, and...
and VA group elements. Cs2AgBiBr6 and Cs2NaBiI6 are conversion elements commonly used in photovoltaic applications.9 Cs2AgBiBr6 has an indirect band gap of 1.95 eV and possesses excellent stability against moisture and temperature, but starts degrading after a few weeks.

2. LEAD-FREE TRIVALENT HALIDE PEROVSKITES WITH A3B2X9 STOICHIOMETRY

In addition to improving the encapsulation of perovskites, another option is to replace Pb with other nontoxic inorganic elements. Beyond group 14 elements, two of group 15 metals in the periodic table, bismuth (Bi) and antimony (Sb), have also been studied for replacing lead (Pb) in the solar-energy-absorbing materials. Bi- and Sb-based perovskites have better chemical and photochemical stability.10,11 In this perspective paper, we are interested in reporting types of A3B2X9 perovskites. We studied the structure stability and applications of various compounds based on Bi and Sb. In the case of bismuth, a large series of compositions have been reported, including Cs3Bi2I9 (X = I, Cl, Br)12–16 and MA3Bi2I9,17,18 and in the case of antimony, stable compounds MA3Sb2I9,19–21 Cs3Sb2I9,11,22,23 and Rb3Sb2I9,24 were reported.

2.1. Bismuth (Bi)-Based Trivalent Halide Perovskites. Bismuth (Bi) is closer to lead (Pb) in the periodic table and shows a similar electronic configuration to Pb. These perovskites can transform into zero-dimensional dimers of face-sharing BX6 octahedra (space group P63/mmc) when A-site cations are substituted with large organic molecules such as CH3NH3+. Among all of the reported bismuth-based perovskites, organic–inorganic hybrid bismuth halide MA3Bi2I9 is the most studied polymorph type. Öz et al. fabricated thin films of zero-dimensional methylammonium iodide bismuthate (CH3NH3)Bi2I7 perovskite using a single-step spin-coating approach. It was found that (CH3NH3)Bi2I9 has a hexagonal space group P63/mmc. Owing to the trivalent state of Bi3+, the solid structure of MA3Bi2I9 features two face-sharing 0D perovskite structures, which is constructed by the MA+ surrounding binuclear octahedral (Bi2I6)3- clusters, and all of these are interlinked via hydrogen bonding.15,17 By studying the electronic structure and optical properties, the first...
excitonic peak for the MA$_3$Bi$_2$I$_9$ light absorber was observed at 2.45 eV. This was large for photovoltaic applications.\textsuperscript{10} The layered-solution crystal-growth method was used to obtain high-quality single crystals of MA$_3$Bi$_2$I$_9$. The Bi$_6$I$_6$ octahedra in MA$_3$Bi$_2$I$_9$ are linked by face-sharing, while one-third of the octahedral B$_3^+$ sites are vacant to maintain charge neutrality. At room temperature, MA$_3$Bi$_2$I$_9$ has a high dielectric constant. It has been observed that the nature of MA$_3$Bi$_2$I$_9$ changed with temperature variation. The antipolar nature observed at 300 K exhibited the hexagonal space group $P\overline{6}_3/mmc$. At the temperatures of 160 and 143 K, the structure was found to be transformed from the hexagonal space group $P\overline{6}_3/mmc$ to the monoclinic space groups $C2/c$ and $P2_1$.\textsuperscript{11,12} Kim et al. reported similar lead-free hybrid perovskites like A$_3$B$_2$X$_9$ with different compositions (A = Cs, MA, FA, EA; B = As, Sb, Bi; X = Cl, Br, I), where MA is methylammonium, FA is formamidinium, and EA is ethylammonium. The crystal structures of A$_3$B$_2$X$_9$ were observed in two types of hexagonal $P\overline{6}_3/mmc$ (dimer) and trigonal $P\overline{3}m1$ (layer) structures,\textsuperscript{11,12} as shown in Figure 1. The materials Cs$_3$Bi$_2$I$_9$, MA$_3$Bi$_2$I$_9$, and FA$_3$Bi$_2$I$_9$ have been reported to be an indirect band gap, and the crystal structure for EA$_3$Bi$_2$I$_9$ has not been reported yet. The optical band gap of MA$_3$Bi$_2$I$_9$ was reported to be 1.94–2.26 eV. The band gap can be tuned from the A-site and B-site substitution; the B-site substitution was very difficult due to simultaneously being influenced by the electronegativity difference and the B–X–B angle.\textsuperscript{11,26} Zhang et al. designed a derivative MP$^+$T$^-$BiI$_6$ (MP$^+$ = 4-methylpiperidinium; T$^-$ = I$_3^-$) from MP$^+$Bi$_2$I$_9$, and they found an improvement in the band gap when using it as a hybrid perovskite. To obtain MP$^+$T$^-$BiI$_6$, they evaporated a mixture, containing 4-methylpiperidine (0.99 g, 10 mmol) and Bi$_2$O$_3$ (1.16 g, 2.5 mmol) in 30 mL of HI (47%) solution at room temperature, and after a few days of reaction, red needle crystals of MP$^+$Bi$_2$I$_9$ were obtained. Again, they redissolved them in an oxidized hydroiodic acid solution and after a few days of slow evaporation reaction, brownish bulk crystals were obtained. MP$^+$T$^-$BiI$_6$ adopted a zero-dimensional (0D) perovskite-like structure that exhibited the centrosymmetric space group of $Pnm$. For this new derivative, the MP$^+$T$^-$BiI$_6$ band gap was found to be 1.56 eV, which was lesser than the band gap of MP$^+$Bi$_2$I$_9$ (1.9 eV).\textsuperscript{19} The partial exchange of iodide to chloride ions in the MA$_3$Bi$_2$I$_9$ perovskite led to the new halogenobismuthate(III) semiconductor (CH$_3$NH$_3$)$_6$BiI$_5$.2$^{22}$Cl$_{3.78}$, which exhibited a different crystal structure. Experimentally and theoretically, the band gaps were obtained at 2.25 and 2.50 eV.\textsuperscript{27}
Apart from the use of MA$_3$Bi$_2$I$_9$ perovskite as a light absorber in solar cells, this can be used to fabricate an electrochemical double-layer capacitor and used as a photocatalyst for hydrogen production.\textsuperscript{17,18} An MA$_3$Bi$_2$I$_9$-based electrochemical double-layer capacitor was fabricated by Pious et al. in 2007. They obtained a maximum areal capacitance of 5.5 mF at a scan rate of 5 mV s$^{-1}$, and this was assumed to be the highest value for a hybrid perovskite-based capacitor.\textsuperscript{17} Guo et al. prepared MA$_3$Bi$_2$I$_9$ using a simple hydrothermal route and characterized its photocatalytic activity. For MA$_3$Bi$_2$I$_9$, the photocatalytic rate for H$_2$ production was obtained at 12.19 $\mu$mol g$^{-1}$ h$^{-1}$. When platinum (Pt) was deposited on the surface of MA$_3$Bi$_2$I$_9$ as a cocatalyst, the photocatalytic rate increased. The MA$_3$Bi$_2$I$_9$/Pt sample, which was prepared with 40 mg of MA$_3$Bi$_2$I$_9$ and 2 mg of H$_2$PtCl$_6 \cdot 6$H$_2$O, showed an excellent photocatalytic rate (169.21 $\mu$mol g$^{-1}$ h$^{-1}$) for H$_2$ production 14 times that of MA$_3$Bi$_2$I$_9$.\textsuperscript{18}

Bismuth-based lead-free hybrid perovskites showed good stability under atmospheric conditions but poor efficiency for photovoltaic applications. The efficiency can be increased by fabricated thin films of MA$_3$Bi$_2$I$_9$ perovskite with TiO$_2$ layers.\textsuperscript{28,29} Ahmad et al. have reported a one-dimensional (1D)-polymeric chain-based [(CH$_3$NH$_3$)$_3$BiCl$_6$]n perovskite.\textsuperscript{28} The 1D layers of MA$_3$Bi$_2$X$_9$ (X = Cl, I) can be prepared by single-step spin-coating and the two-step soaking-assisted method.\textsuperscript{30,31} To achieve better photovoltaic performances, MA$_3$Bi$_2$I$_9$ was fabricated with all three configurations of TiO$_2$ (planar, mesoporous brookite, and anatase TiO$_2$).\textsuperscript{30} The samples of the MA$_3$Bi$_2$I$_9$ perovskite prepared on the anatase TiO$_2$ mesoporous layer showed good film coverage and reduced junction resistance as well as charge recombination, giving values better than those on planar and brookite mesoporous layers.\textsuperscript{33}

Moreover, all inorganic bismuth iodide perovskites A$_3$Bi$_2$X$_9$ (A = Cs, Rb; X = I, Br) have been reported in refs 13, 34, 35. Further, the main issue with A$_3$Bi$_2$X$_9$ was its large band gap, which was relatively large to be used in a single-junction solar cell (1.9~2.2 eV for Cs$_3$Bi$_2$I$_9$). It has been demonstrated that Cs-based perovskites are indirect, while Rb-based ones have a direct band gap. A theoretical and experimental study was carried out to reduce the band gap by alloying metal substitution.\textsuperscript{2.2} The In (indium)- and Ga (gallium)-doped Bi-based perovskites were obtained through density functional theory (DFT) calculations, band structures, and electronic properties determined using the Vienna ab initio simulation package (VASP). The spin–orbit coupling was used to compare various hybrid perovskites. The Cs$_3$Bi$_2$I$_9$ has a hexagonal structure space group $P6_3/mmc$ similar to MA$_3$Bi$_2$I$_9$. The band gap of Cs$_3$Bi$_2$I$_9$ was found to be indirect. When the Cs$_3$Bi$_2$I$_9$ perovskite was doped with Ga and In, the structure exhibited a direct band gap because the valence band maximum shifted near the $\Gamma$-point. When Bi was replaced with Ga, the band gap of the Cs$_3$Bi$_2$Ga$_x$I$_9$ space group $P6_3/mmc$ ($P3m1$ Figure 2) was obtained as 1.60/1.20 eV, which was lower than that of Cs$_3$Bi$_2$I$_9$ by 0.65/0.54 eV, while in the case of Cs$_3$Bi$_2$In$_x$I$_9$ the band gap was smaller than that of Cs$_3$Bi$_2$Ga$_x$I$_9$ by 0.3 eV.\textsuperscript{12,14} The valence band was formed due to Ga $p$ and In $p$ having a lower energy than the valence band maximum (VBM), and conduction bands were formed with the hybridization of I $sp$, Bi $p$, and In/Ga $s$ orbitals. It has been demonstrated that the Cs$_3$Bi$_2$I$_9$ perovskite with a $P3m1$ symmetry was more appropriate for realizing a lower band gap.\textsuperscript{36} The A$_3$Bi$_2$X$_9$ perovskites can be converted into double perovskites. Recently in 2020, Peedikakkandy et al. prepared a three-dimensional (3D) Cs$_3$NaBi$_2$I$_9$ double perovskite by incorporating an alkali metal sulfide group Na$_2$S in Cs$_3$Bi$_2$I$_9$, the results showed that the band gap reduced, and this was introduced as a new family member of lead-free hybrid perovskites. The ionic radius of Na$^+$ (102 pm) closely agreed with that of Bi$^{3+}$ (103 pm). In ternary perovskites such as Cs$_3$Bi$_2$I$_9$, the valence band has a strong Bi $6s$ and I $5p$ antibonding character, whereas the conduction band is predominantly formed through the Bi $6p$ states. The Cs$_3$Bi$_2$I$_9$ perovskite was p-type in nature, while the Cs$_3$NaBi$_2$I$_9$ double perovskite had an n-type nature.\textsuperscript{13} Another Bi-based perovskite Cs$_3$Bi$_2$Br$_9$ has been reported in refs 37, 38. The structure of pure Cs$_3$Bi$_2$Br$_9$ was found to be crystallized in a P1(1)-monoclinic form, and it possesses both direct and indirect band gaps for an optically allowed transition; the direct/indirect band gap of Cs$_3$Bi$_2$Br$_9$ was found to be 2.67/2.62 eV. The Cs$_3$Bi$_2$Br$_9$ perovskite belongs to the hexagonal phase with space group $P3m1$. First, DFT was used for structure investigation of the bulk Cs$_3$Bi$_2$Br$_9$ perovskite; the valence band was composed of Br $4p$ orbitals to the conduction band (CB) majorly contributed by Bi $6p$ orbitals hybridized with a small amount of Br $4p$ orbitals. Further, the given information was demonstrated by optical transient absorption (OTA) and X-ray transient absorption (XTA) spectroscopies.\textsuperscript{34}

The other possibility was carried out for reducing the band gap of Bi-based perovskites by alloying another halide at the Bi$^{3+}$ site.\textsuperscript{38} The trivalent cations form A$_3$Bi$_2$X$_9$ structures with 2/3 occupancy of the B sites and 1/3 remaining vacant of the same A$_3$Bi$_2$X$_9$ perovskite formula. Ghosh et al. in 2020, reported a Cs$_3$Bi$_2$Br$_{1-x}$I$_x$ perovskite and observed electronic and optical properties at different ratios of Br to I. The radius of Br$^-$ is lower than that of I$^-$, resulting in reduced d-spacing. It has been observed that the phase did not change until 40% I$^-$ alloying (Cs$_3$Bi$_2$Br$_{5.4}$I$_{3.6}$). The replacement of terminal Bi–I bonds by Bi–Br bonds in BiI$_6$ octahedra alloyed BiI$^{3+}$/Br$^-$ octahedra. For Cs$_3$Bi$_2$Br$_{4.5}$I$_{1.5}$ emission, maxima were observed at 486 nm, and the photocurrent gain value was found to be approximate 12, which is larger than Cs$_3$Bi$_2$Br$_9$.\textsuperscript{37} The substitution of Pb$^+$ in layered Cs$_3$Bi$_2$Br$_9$ halide perovskites enhanced the visible-light absorption. Recently in 2020, Roy et al. synthesized a Pb-substituted Cs$_3$Bi$_2$Br$_9$ bulk perovskite by the chemical reprecipitation method. Pb has a +2 oxidation state, whereas Bi has a +3 oxidation state; thus, when Bi is replaced with Pb, it leads to charge imbalance in the compound, creating new states above the valence band because of Pb $s$ and Br $p$ antibonding orbitals. The crystal structure of Cs$_3$Bi$_2$Br$_9$ remained unchanged after Pb substitution because the radius of Pb (1.19 Å) is nearly equal to that of Bi (1.03 Å). It was observed that the size of the Pb-substituted Cs$_3$Bi$_2$Br$_9$ perovskite increased from 52 to 115 nm when the Pb concentration increased, while the band gap reduced from 2.62 to 2.23 eV on increasing the Pb concentration.\textsuperscript{38}

A new nontoxic Bi-based all-inorganic semiconductor Rb$_2$Ag$_2$BiBr$_9$ was reported by Sharma et al. in 2019. This was the first compound discovered in the quaternary Rb–Ag–Bi–Br phase diagram that adopted a new structure (Pearson’s code oP32). According to density functional theory (DFT) predictions, this compound provided a nearly direct band gap (slightly indirect) of 1.69 eV. Moreover, Rb$_2$Ag$_2$BiBr$_9$ was stable in ambient air for several weeks.\textsuperscript{35}
In Table 1, we have provided the chemical formula, space group, $E_{\text{gap}}$ (eV), $V_{\text{oc}}$(V), PCE (%), $J_{\text{sc}}$ (mA cm$^{-2}$), and refs for selected trivalent and mixed double halide lead-free hybrid perovskites. The table includes the following entries:

| B cation          | perovskites               | space group | $E_{\text{gap}}$ (eV) | $V_{\text{oc}}$(V) | PCE (%) | $J_{\text{sc}}$ (mA cm$^{-2}$) | refs |
|-------------------|---------------------------|-------------|-----------------------|-------------------|---------|-------------------------------|------|
| trivalent         | (MA)$_3$Bi$_3$I$_9$       | P6$_3$/mmc  | 1.9–2.2               | 0.66              | 0.12    | 0.52                          | 10, 17, 47 |
|                   | Cs$_3$Bi$_3$I$_9$         | P6$_3$/mmc  | 2.2                   | 0.85              | 1.09    | 2.15                          | 47   |
|                   | (MA)$_3$Sb$_2$I$_9$       | P6$_3$/mmc  | 2.0/2.5               | 0.89              | 0.5     | 1                             | 11, 48 |
|                   | Cs$_3$Sb$_2$I$_9$         | P6$_3$/mmc/P3m1 | 2.05             | 0.31              | 0.01    | 0.52                          | 49   |
|                   | Cs$_3$SbBr$_3$            |             | 2.36                  |                   |         | 1                             | 44   |
|                   | Rb$_3$Sb$_2$I$_9$         | Plc1        | 2.24                  | 0.55              | 0.66    | 2.11                          | 24, 50 |
|                   | (C$_6$H$_{14}$N)$_3$Bi$_2$I$_9$ |             | 2.02                  |                   |         |                                | 19   |
|                   | EA$_3$Bi$_3$I$_9$         |             | 2.03                  |                   |         |                                | 11   |
| double halide     | Cs$_3$AgBiBr$_6$          | Fm$ar{3}$m | 1.95, 2.19            | 1.01              | 2.2     | 3.19                          | 51–53 |
|                   | Cs$_3$AgBiCl$_6$          | Fm$ar{3}$m | 2.77, 2.3–2.5         |                   |         |                                | 52, 54 |
|                   | Cs$_3$AgBiI$_3$           | Fm$ar{3}$m | 1.75                  |                   |         |                                | 55   |
|                   | Cs$_3$AgSbCl$_6$          | Fm$ar{3}$m | 2.54                  |                   |         |                                | 56   |
|                   | Cs$_3$NaBiI$_6$           | P6$_3$/mmc  | 1.66                  | 0.47              | 0.42    | 1.99                          | 57, 58 |
|                   | Cs$_3$AgInCl$_6$          | Fm$ar{3}$m | 3.3                   |                   |         |                                | 59, 60 |
|                   | Cs$_3$AgFeCl$_6$          | Fm$ar{3}$m | 1.65                  |                   |         |                                | 61   |
|                   | Cs$_3$AgSbBr$_6$          | Fm$ar{3}$m | 1.46                  | 0.35              | 0.01    | 0.08                          | 62, 63 |

2.2. Antimony (Sb)-Based Trivalent Halide Perovskites. Antimony is a trivalent ($\text{Sb}^{3+}$) cation that possesses a similar electronic configuration as divalent $\text{Pb}^{2+}$. Sb is expected to be nontoxic, which exhibits a similar atomic structure and properties to those of Bi. Sb-based perovskites like MA$_3$Sb$_2$I$_9$ for achieving the narrowest band gap, and it could be prepared by partial substitution of Sb(III) by Pb(II) in the MAPbI$_3$ – MA$_3$Sb$_2$I$_9$ interface. It was observed that the substituted Sb does not fully incorporate into the structure but rather acts as a surface layer.21

In Table 1, we have provided the chemical formula, space group, $E_{\text{gap}}$ (band gap), $V_{\text{oc}}$(open-circuit voltage), PCE (power conversion efficiency), and $J_{\text{sc}}$ (short-circuit current density) of nontoxic trivalent and double halide perovskites. Similarly, Sb-based Cs$_3$Sb$_2$I$_9$ and Rb$_3$Sb$_2$I$_9$ perovskites have been reported for photovoltaic applications.32,60 The material Rb$_3$Sb$_2$I$_9$ was found in a distorted monoclinic layered structure with space group $P\overline{2}_1/n$, and the band gap was obtained to be 2.03 eV. In the case of Cs$_3$Sb$_2$I$_9$ (1.89 eV), both structures can be formed either dimer or layer. These materials have demonstrated high resistivities, ranging from 1010 to 1012 $\Omega$ cm. Recently in 2020, Pradhan et al. reported a new Cs$_3$Sb$_2$Cl$_9$ perovskite. Using the XRD study, the compound Cs$_3$Sb$_2$Cl$_9$ was found in two phases: trigonal and orthorhombic; the trigonal phase existed at temperatures below 85 $^\circ$C, while the orthorhombic phase existed above 130 $^\circ$C. They observed that at a high temperature (300 $^\circ$C), the orthorhombic phase completely transformed to the trigonal phase. The phase of Cs$_3$Sb$_2$Cl$_9$ can also be transformed by Bi substitution. Experimentally, the indirect band gap for the trigonal/orthorhombic phase was observed to be 2.89/2.86 eV, while theoretically, it was observed to be 2.41/2.39 eV.64 Moreover, Sb-based perovskites have been used in light-emitting diodes (LEDs). Singh et al. synthesized Sb-based 2D perovskites Cs$_3$Sb$_2$Cl$_9$ and Cs$_3$Sb$_2$Br$_9$ using the vapor-anion-exchange method. The materials Cs$_3$Sb$_2$Cl$_9$ and Cs$_3$Sb$_2$Br$_9$ showed n-type conductivity. They reported the first lead-free perovskite LED based on 2D Cs$_3$Sb$_2$I$_9$ as the emitter. The device prepared by the Cs$_3$Sb$_2$I$_9$ film as the active layer provided a red emission.23 A colloidal method was used to fabricate Sb-based 2D lead-free perovskites. 1-Dodecanol is a polar solvent that can be used as a solvent and a capping agent to enhance the size uniformity of perovskites.25,34,54 Wojciechowska et al. reported a new 2D lead-free hybrid ferroelectric (pyrrolidinium)$_2$[Sb$_2$Cl$_4$]. It was found that (C$_6$H$_{14}$NH$_2$)$_2$[Sb$_2$Cl$_4$] has a trigonal $R3m$ crystal structure and it is built up of [Sb$_2$Cl$_4$]$^{2–}$ infinite layers, composed of corner-sharing SbCl$_6$ octahedra, and pyrrolidinium counterions balance the negative charge of the layers.55 2D and 3D materials are more desirable for photovoltaic applications than 0D materials given their lower band gap and smaller exciton banding energy. The optoelectronic properties of perovskites can be changed with tuning by halide and A- and B-site substitution. Correa-Baena et al. in 2018 reported A$_2$Sb$_3$I$_7$ perovskites and observed changes in optoelectronic properties by exchanging the A-site substitution. It was observed that Cs$_3$Sb$_2$I$_9$ formed a 0D
structure surrounded by SbI₆ octahedra, whereas Rb₃Sb₂I₉ formed a 2D layer structure, as shown in Figure 3. The thin films of compounds Cs and K showed indirect band gaps of 2.43 and 2.03 eV, while thin films of Rb showed a direct band gap of 2.02 eV. They also used DFT calculations and obtained band gaps for the Cs, Rb, and K compounds to be 1.89, 1.99, and 2.03 eV, respectively. The highest photocurrent efficiency (0.76%) was observed for Rb₃Sb₂I₉. However, in the dimer phase, the Cs₃Sb₂I₉ perovskite has a low charge transport efficiency; various techniques have been developed to transform it into a layered structure. The Rb cations can be accommodated by layered modification (Figure 3). In this paper, the band gap of Rb₃Sb₂I₉, which was found to be direct, was 1.98 eV.¹⁴

Unlike Bi- and Sb-based materials, some new trivalent materials Rb₃In₂I₉, Cs₃In₂I₉, and Cs₃Ga₂I₉ have been reported by Jain et al. The DFT calculations were carried out to analyze crystal structures. They used GGA and HSE06 calculations to predict band structures. The band gaps of Rb₃In₂I₉, Cs₃In₂I₉, and Cs₃Ga₂I₉ materials by HSE06 calculations were obtained to be 2.05, 2.12, and 1.72 eV, respectively. The GGA calculations showed a lower band gap because it is not fully described the many-body effect.²⁵

3. LEAD-FREE MIXED DOUBLE HALIDE PEROVSKITES WITH A₂MM’X₆ STOICHIOMETRY

Organic–inorganic lead halide perovskites have reached an efficiency of 25.5%. However, toxicity due to the presence of lead, and instability at high temperature and humidity, has impelled researchers to look for more stable and lead-free alternatives, with double halide perovskites being one such family of perovskites. They are of the form A₂MM’X₆, where A is a monovalent cation, M is a trivalent metal cation, M’ is a monovalent metal cation, and X is a halide anion.

3.1. Experimental Status of A₂MM’X₆ Stoichiometry-Based Mixed Double Halide Perovskites. In 2016, Slavney et al. synthesized crystals of Cs₂AgBiBr₆ using a concentrated HBr solution that contained CsBr, AgBr, and BiBr₃. The space group was Fm̅3m with a red-orange color of the crystal. The lattice parameter was 11.25 Å. The indirect band gap was measured to be 1.95 eV and the direct band gap to be 2.21 eV. In the same year, McClure et al. synthesized Cs₂AgBiX₆ (X = Br, Cl) by both solid-state and solution routes. However, excellent phase purity was observed for samples synthesized via the solution process. The space group was Fm̅3m with lattice parameters 11.2711 Å (X = Br) and 10.7774 Å (X = Cl) and band gaps 2.19 eV (X = Br) and 2.77 eV (X = Cl) measured by diffuse reflectance. Later in 2018, Creutz et al. synthesized colloidal nanocrystals of Cs₂AgBiX₆ (X = Br, Cl) using the hot injection approach. They also synthesized Cs₂AgBiCl₆ for the first time by anion-exchange reactions. For the complete anion-exchange reaction, TMSX (TMS = trimethylsilyl) reagents were found to be efficient. The XRD pattern of Cs₂AgBiI₆ shows that it has a lattice parameter of 12.09 Å with space group Fm̅3m. The band gap observed was 1.75 eV. Another way of synthesizing Cs₂AgBiX₆ nanocrystals is by the antisolvent recrystallization method. In this method, Yang et al. dissolved CsBr, AgBr, and BiBr₃ in a dimethyl sulfoxide (DMSO) solvent to form a precursor solution. To precipitate the nanocrystals, isopropanol was used as the antisolvent. Volonakis et al. experimentally synthesized by the solid-state reaction as well as computationally designed Cs₂AgBiCl₆ using first-principles calculations in the framework of density functional theory (DFT) in local density approximation (LDA). The space group was again found to be Fm̅3m. The experimentally and computationally predicted lattice parameters were found to be 10.78 and 10.50 Å, respectively. The optical indirect band gap was found to be in the range of 2.3–2.5 eV estimated from the optical absorption spectrum and the Tauc plot. In 2017, Volonakis et al. also synthesized powdered Cs₂AgInCl₆ by precipitating InCl₃, AgCl, and CsCl in HCl. Unlike the other double perovskites, this system had a direct band gap. Experimentally and computationally, the lattice parameters were found to be 10.47 and 10.20 Å, respectively. The experimentally and computationally predicted direct band gaps were found to be 3.3 eV and (2.7 ± 0.6) eV, respectively. The space group for this system was Fm̅3m as well. Zhou et al. synthesized microcrystals of Cs₂AgInCl₆ by a hydrothermal method. The lattice parameter was found to be 10.4805 Å. The experimental band gap was reported to be 3.23 eV via UV–vis measurement and computationally (using the HSE06 functional) to be 3.33 eV. Tran et al. synthesized polycrystals of both Cs₂AgInCl₆ and Cs₂AgSbCl₆ through solid-state techniques, which involved combining AgCl, CsCl, and InCl₃(SbCl₅) and heating at temperatures of 400 and 210 °C, respectively. Both the structures were cubic having space group Fm̅3m with lattice parameters 10.469 and 10.646 Å, respectively. Cs₂AgSbCl₆ was found to be an indirect band-gap

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Figure 3. Schematic showing the influence of the A cation size on the structure of A₃Sb₂X₆ (A = Cs, Rb). Reprinted with permission from ref 24. Copyright 2016 American Chemical Society.
semiconductor, whereas Cs$_2$AgInCl$_6$ had a direct band gap. The UV−vis diffuse reflectance spectra reported the indirect band gap of Cs$_2$AgSbCl$_6$ to be 2.54 eV and the direct band gap of Cs$_2$AgInCl$_6$ to be 3.53 eV. The nature of the band gap was validated by DFT-LDA calculations taking into account the spin−orbit coupling (SOC) effect. Another double perovskite system Cs$_2$NaBiI$_6$ was first reported by Zhang et al. The crystals of Cs$_2$NaBiI$_6$ were synthesized using the hydrothermal process at 120 °C for 2 h. After cooling, the crystals were obtained. It was further washed in DI water and centrifuged to obtain the final product. It belongs to the space group P6$_3$/mmc having a band gap of 1.66 eV. Although Cs$_2$AgBiX$_6$ single crystals, polycrystals, and nanocrystals could be synthesized successfully, fabricating good-quality films was inhibited because of the low solubility of precursors. In 2017, Greul et al. successfully synthesized high-quality films of Cs$_2$AgBiBr$_6$ by synthetic routes and also incorporated them in working devices. In this method, CsBr, AgBr, and BiBr$_3$ are dissolved in DMSO to form a precursor solution. The solution along with the substrate is preheated at 75 °C before spin-coating. After spin-coating, the substrate is annealed at 285 °C under ambient conditions for 5 min. This led to the formation of the desired Cs$_2$AgBiBr$_6$ film. In the same year, Wu et al. synthesized a good-quality film of Cs$_2$AgBiBr$_6$ by low-pressure-assisted solution processing under ambient conditions. In this case, the solution is first spin-coated and then transferred to a low-pressure chamber having 20 Pa pressure. The residual solvent is removed by annealing at 200 °C leading to the formation of a uniform thin film.

3.2. Stability Determination of A$_2$MM$'$X$_6$ Stoichiometry-Based Mixed Double Halide Perovskites. One of the major reasons for replacing double halide perovskites with lead-based perovskites is the stability in the former case. The structural stability can be quantitatively determined by Goldschmidt’s tolerance factor ($t$) and octahedral factor ($\mu$). Both of these factors depend on the Shannon ionic radii of A, M, M$'$, and X. Goldschmidt postulated that perovskites arrange so that “the number of anions surrounding a cation tends to be as large as possible, subject to the condition that all anions touch the cation” (ref 70). This limits the value of $t$ and $\mu$ and constitutes the “no-rattling” principle. $t$ and $\mu$ can be expressed in the following equations

$$t = \frac{R_A + R_X}{\sqrt{2}(R_{\text{avg}} + R_A)}$$  \(1\)

$$\mu = \frac{R_{\text{avg}}}{R_X}$$  \(2\)

where $R_{\text{avg}} = (R_B + R_{B'})/2$, with $R_A$ and $R_X$ being the Shannon ionic radii of A and X, respectively. For the perovskite to be in the stable structure, $t$ should be between 0.825 and 1.059, whereas $\mu$ should be between 0.442 and 0.895.

Recently, Bartel et al. reported a new tolerance factor ($\tau$), which is given by
Rb$_2$AgCrBr$_6$, K$_2$AgCrBr$_6$, Cs$_2$AgCrCl$_6$, and Cs$_2$AgCrI$_6$ are substitutions due to its stability, but its indirect band gap limits its promising double halide perovskite for photovoltaic applications. In this section, we see how by their use in varied applications. One of the ways to tune the band gaps is by substitution. In this section, we see how by substitution, one can successfully tune the band gaps to optimum value and also modulate the nature of various double halide perovskites, one can successfully tune the indirect band gaps, they show very low efficiency. This limits perovskites are stable and promising candidates for various applications.  

$$
\tau = \frac{R_X}{R_{avg}} - n_A \left( \frac{R_A}{R_{avg}} \right) \ln \left( \frac{R_A}{R_{avg}} \right)
$$

where $n_A$ is the oxidation state of the A-site cation. $\tau$ should be less than 4.18 to obtain a stable structure. 

$(t, \mu, \tau)$ for Cs$_2$AgBiBr$_6$ is (0.86, 0.56, 4.21), and for Cs$_2$AgBiCl$_6$ it is (0.87, 0.60, 4.07). For Cs$_2$AgBi$_{1-x}$Cl$_x$ mixed halide double perovskites, $(t, \mu, \tau)$ are in the ranges (0.86—0.87, 0.56—0.60, 4.07—4.21). $(t, \mu, \tau)$ for Cs$_2$AgCrBr$_6$, Rb$_2$AgCrBr$_6$, K$_2$AgCrCl$_6$, and Cs$_2$AgCrI$_6$ are (0.96, 0.45, 4.04), (0.92, 0.45, 4.14), (0.90, 0.45, 4.22), (0.97, 0.49, 3.87), and (0.94, 0.40, 4.31), respectively.

### 3.3. Effect of Substitution in A$_2$MM$^+$X$_6$ Stoichiometry-Based Mixed Double Halide Perovskites

Double halide perovskites are stable and promising candidates for various photovoltaic applications. However, due to their wide and indirect band gaps, they show very low efficiency. This limits their use in varied applications. One of the ways to tune the band gaps is by substitution. In this section, we see how by substituting different elements like Sb, In, Bi, Tl, Mn, and Fe in double halide perovskites, one can successfully tune the band gaps to optimum value and also modulate the nature of the band gap.

#### 3.3.1. Effect of Sb, In, and Bi Substitution

Cs$_2$AgBiBr$_6$ is a promising double halide perovskite for photovoltaic applications due to its stability, but its indirect band gap limits its efficiency. Du et al. performed band-gap engineering of Cs$_2$AgBiBr$_6$ by substituting Sb and In in place of Bi. They successfully synthesized Cs$_2$AgBi$_{1-x}$In$_x$Br$_6$ ($x = 0$, 0.25, 0.50, and 0.75) and Cs$_2$AgBi$_{1-x}$Sb$_x$Br$_6$ ($x = 0$, 0.125, and 0.375). The In and Sb substituted systems having concentrations greater than $x = 0.75$ and $x = 0.375$, respectively, were found to be unstable and hence could not be synthesized. With the increase in concentration of substitution, it was observed that the lattice parameters decreased linearly following Vegard’s law. The band gap for Cs$_2$AgSbBr$_6$ is 1.58 eV higher than that of Cs$_2$AgBiBr$_6$. The band gap increased from 2.12 to 2.27 eV with an increase in concentration. For Sb substituted Cs$_2$AgBiBr$_6$, the band gap decreased from 2.12 to 1.86 eV with an increase in concentration. Band structures were also calculated by DFT (HSE06 + SOC) for the substituted systems. The band gap for Cs$_2$AgSbBr$_6$ (Figure 4c) was found to be 1.67 eV. The band gap was lowered by 0.04 eV due to Sb substitution, which was in accordance with the experimental results. The band gap for Cs$_2$AgBiBr$_6$ (Figure 4c) was found to be 2.15 eV. The band gap for Cs$_2$AgSbBr$_6$ was 0.06 eV less than the band gap of Cs$_2$AgBiBr$_6$. This contradicted the experimentally observed band gap where it increased with an increase in the In concentration. This is due to the ordered BiBr$_6$ octahedra in DFT calculation, which is not the case experimentally. For Cs$_2$AgBi$_{0.75}$In$_{0.25}$Br$_6$, the band gap was found to be 2.28 eV, which is in accordance with the experimental trend.

Transition of band gap from indirect to direct was also observed for Cs$_2$AgSb$_{1-x}$In$_x$Cl$_6$ by Tran et al. Cs$_2$AgSbCl$_6$...
and Cs$_2$AgSb$_{0.5}$In$_{0.5}$Cl$_6$ have indirect band gaps of 2.54 and 2.81 eV, respectively. For $x = 0.4$ and 0.2, i.e., Cs$_2$AgSb$_{0.4}$In$_{0.6}$Cl$_6$ and Cs$_2$AgSb$_{0.2}$In$_{0.8}$Cl$_6$, respectively, the band gaps become direct in nature with values of 2.92 and 3.06 eV, respectively. Cs$_2$AgInCl$_6$ was also observed to have a direct nature of band gap. As the concentration of Sb increased, it was observed that the nature of the band gap altered from direct to indirect with a decrease in the value. The band structures of Cs$_2$AgSbCl$_6$ and Cs$_2$AgInCl$_6$ were calculated using local density approximation (LDA) considering spin–orbit coupling (SOC). The SOC effect was more prevalent for Cs$_2$AgSbCl$_6$ rather than Cs$_2$AgInCl$_6$ as Sb shows greater relativistic effects than In. Due to the SOC effect, it was observed that the first conduction band of Cs$_2$AgSbCl$_6$ is split at the energy level of 0.6 eV at the $\Gamma$ point. From the projected density of states (DOS) of both structures, it was seen that the Ag d and Cl p orbitals contributed to the valence band edge. For Cs$_2$AgSbCl$_6$, the conduction band is mainly contributed by the Sb 5p orbitals. However, for Cs$_2$AgInCl$_6$, the conduction band is contributed by In s and Cl p orbitals. As the concentration of Sb increases, the Sb 5s orbital contribution increases in the valence band and the In 5s orbital contribution decreases in the conduction band. This leads to the shift from direct to indirect band gap with the incorporation of Sb.

Codoping of Bi$^{3+}$ with lanthanoids like Er$^{3+}$ and Yb$^{3+}$ in the double halide perovskite Cs$_2$AgInCl$_6$ shows promising applications in optical fiber communications, near-infrared (NIR) LEDs, and NIR sensors. Ln$^{3+}$ (Ln = Er and Yb)-doped double perovskites by Arfin et al. showed a weak near-infrared emission intensity and a high excitation energy ($\leq$350 nm). However, after codoping it with Bi$^{3+}$, the projected density of states (PDOS) at the band edges got modified, which was responsible for the new optical absorption peak at a lower energy (372 nm), as shown in Figure 5. This energy that is absorbed gets transferred to the Ln$^{3+}$ f-electrons, promoting the NIR dopant emissions. The PDOS of pristine Cs$_2$AgInCl$_6$ shows hybridization of Ag 5s, Cs 6s, and Cl 3p orbitals in the conduction band as well as a deeper valence band regime. However, for Bi$^{3+}$-doped (12.5 atom %) samples, the contribution of Bi at the band edges of both the valence band maximum and the conduction band minimum is significant. This leads to the change in the optical transitions near the band-gap energies.

3.3.2. Effect of Tl, Mn, and Fe Substitution. Band-gap tuning can also be done by substituting Tl$^{3+}$ in Cs$_2$AgBiBr$_6$, which leads to a carrier lifetime similar to that of CH$_3$NH$_3$PbI$_3$. Slavney et al. substituted Tl$^{3+}$ to tune the band gap of the double perovskite Cs$_2$AgBiBr$_6$. DFT-calculated energy loss/gain owing to Tl substitution showed that Tl$^{3+}$ substitution at...
the Bi site is not favorable with energy $\Delta E = 0.7$ eV. However, for substitution at the Ag site, the energy was $\Delta E = -0.05$ eV, which is energetically favorable. Band structure calculations were also performed using the PBE + SOC functional for Cs$_{1-x}$Bi$_x$Tl$_x$Br$_6$, where $x = a + b$. For $x = 0.06$, the band-gap nature shifted from indirect to direct with substitution at the Ag site, as shown in Figure 6A. In VBMs, the Tl s states were found to be above Cs$_2$AgBiBr$_6$ states, leading to the reduction of the band gap. In CBM, there is hybridization of Tl p states with Br p and Bi p orbitals leading to the direct nature of the band gap. However, substituting at the Bi site does not change the nature of the band gap and it remains indirect, as observed from Figure 6B. Substitution of Tl at both Ag and Bi sites leads to the indirect nature of the band gap with a reduction in the band gap as well. Here, the VBM is made up of Tl s orbitals rather than Tl p orbitals, which leads to the indirect nature of the band gap.

Visible-light emission in direct band gap Cs$_2$AgFeCl$_6$ by Mn$^{3+}$ doping was observed by Nandha and Nag. Upon illumination by UV light, a red color emission was observed from the Mn-doped Cs$_2$AgInCl$_6$. The energy absorbed by Cs$_2$AgInCl$_6$ was transferred to the Mn d electrons. The de-excitation of energy from the Mn d electrons resulted in PL with a lifetime of milliseconds. The intensity of PL emission increased with an increase in the concentration of Mn until 1%. With a greater concentration of Mn, the PL intensity decreased due to the possible Mn$^{2+}$-Cl$^{-}$-Mn exchange interactions.

Recently, Yin et al. synthesized stable Cs$_2$AgFeCl$_6$ as well as Cs$_2$AgIn$_{0.76}$Fe$_{0.24}$Cl$_6$. The absorbance of these crystals is in the range of 450–800 nm. This amplifies the PL quantum yield by 167 times. Fe 3d and In 5s states lead to an increase in the carrier transport ability in these systems. From the band structure (Figure 7) analysis, it was observed that as the concentration of In increased, the band gap also increased. Cs$_2$AgFeCl$_6$ and Cs$_2$AgInCl$_6$ showed direct band gaps, but Cs$_2$AgIn$_{0.76}$Fe$_{0.24}$Cl$_6$ showed an indirect band gap. For Cs$_2$AgFeCl$_6$ and Cs$_2$AgIn$_{0.76}$Fe$_{0.24}$Cl$_6$, Fe 3d and Cl 3p orbitals contribute to the VBM. The interaction of Fe and Cl atoms promotes the bichannel carrier transport. Fe 3d orbitals have a slightly higher energy than In orbitals below the Fermi level. This leads to lowering of the VBM with an increase in the concentration of In in the system, and hence, an increase in the band gap was observed.

**4. SUMMARY AND FUTURE OUTLOOK**

In this perspective, we have stressed on different aspects of lead-free perovskite materials, their structure, various optoelectronic properties, and photoconversion efficiency. We have discussed briefly different synthesis techniques like the single-step spin-coating approach, layered-solution crystal growth, two-step soaking-assisted method, etc. The space group and the direct or indirect band gap of perovskite materials are major deciding factors. Here, we have also discussed some of the limitations (toxicity, wide band gap, instability, etc.) and their corrective measures.

Toxicity is the major factor limiting the commercialization of Pb-based perovskites. Another divalent metal substitutes of Pb$^{2+}$, like Sn$^{2+}$, is highly unstable and easily gets converted into
Cs2NaBiI6, and Cs2TiBr6 are perovskites used in the A3M2X9 type can be illustrated through Sb- and Bi-based perovskites. Antimony (Sb)-based perovskite materials have been discussed in this perspective. The FA4GeSbCl12 is a newly discovered double perovskite having a band gap of 1.3 eV.85 Coming out of the stereotypes, di-...
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Perspective

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