Lead-Free Double Perovskite Cs$_2$AgBiBr$_6$: Fundamentals, Applications, and Perspectives

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Cs$_2$AgBiBr$_6$, as a benchmark lead-free double perovskite, has emerged as a promising alternative to lead-based perovskites because of its high stability, non-toxicity, exceptional optoelectronic properties, and multifunctionality. To encourage further research on Cs$_2$AgBiBr$_6$ and its broad applications, in this review, its fundamental properties including the structure-property relation, synthesis, stability, origin of absorption and photoluminescence, electron-phonon coupling, role of defects, charge carrier dynamics, and bandgap modulation are comprehensively emphasized. The recent progress on the wide applications including solar cells, light/X-ray detectors, and ferroelectric/magnetic devices are highlighted. Moreover, the challenges of Cs$_2$AgBiBr$_6$ materials and related applications are discussed and perspectives are provided for guiding the future development of this research area.

1. Introduction: The Emergence of Lead-Free Perovskites

Lead (Pb) halide perovskites, with a general chemical formula of ABX$_3$, where A is a CH$_3$NH$_3$$^+$ (MA$^+$), CH$_3$(NH$_2$)$_2$CH$^+$ (FA$^+$) or Cs$^+$ cation, B is a Pb$^{2+}$ cation and X is Cl$^-$, Br$^-$ or I$^-$ anion, have attracted tremendous attention in both scientific and industrial fields in the last 10 years. Lead-based perovskites have demonstrated exceptional optoelectronic properties such as a suitable and tunable direct bandgap, strong light absorption, long carrier lifetime and diffusion length, small and balanced carrier effective mass, easy solution fabrication, high structural diversity, and high defect tolerance.[1,2] Such remarkable properties make perovskite a versatile material for a wide range of applications such as solar cells, photodetectors, light-emitting devices, photocatalysis, X-ray imaging, lasing and luminescent solar concentrators.[3,4] Among these applications, lead-based perovskite solar cells (PeSCs) are best known, having achieved a state-of-the-art power conversion efficiency (PCE) of 25.5% for a single-junction laboratory-scale device and a 29.5% record PCE for a perovskite/silicon tandem monolithic device.[5] This progress has been achieved through fabricating high-quality perovskite films and optimizing device interface contact to minimize energy losses. Additionally, lead-based perovskite light-emitting diodes (PeLEDs) now have also delivered high external quantum efficiencies (EQEs) over 20% through suppression of non-radiative recombination and improvement of light out-coupling efficiency.[6]

Despite the notable progress in perovskite optoelectronic devices, lead perovskites still suffer from two major issues, i.e., the lack of stability and Pb toxicity. Indeed, lead halide perovskite films are sensitive to ambient conditions (oxygen and water), prolonged illumination, and high temperatures, leading to fast material degradation. Although considerable efforts have been devoted to improving the stability of PeSCs, their lifetime is still far behind the warranty of 25 years for commercial PV modules. Furthermore, for PeLEDs, its operational stability is even worse than PeSCs, with most reported lifetimes ($T_{90}$) generally limited to tens to hundreds of hours, due mainly to ion migration, electrochemical reactions, and interfacial reactions.[7] The toxicity of Pb presents another big obstacle for future commercialization. Pb is a particularly insidious bioaccumulative hazard that has the potential to cause irreversible health problems. While perovskite devices are carefully encapsulated and lead ions are rationally captured by lead-absorbing materials and strictly recycled, the prevention of Pb leakage into the environment cannot be guaranteed.

To tackle these issues, significant efforts have been committed to developing lead-free perovskites, in the hope to combine the impressive optoelectronic properties of lead-based perovskites with high stability and nontoxicity. As the superior properties of lead perovskites originate from the unique electronic configuration of Pb 6$s^2$, divalent tin (Sn$^{2+}$) and germanium (Ge$^{2+}$) in the same group with similar lone pair were first used to replace Pb. However, Sn and Ge-based perovskites show very poor stability because of the rapid oxidation of Sn$^{2+}$ and Ge$^{2+}$ to +4 states. Furthermore, Sn might be even more toxic than Pb for human beings upon dispersion into the environment.[8] An emerging and promising method is to use one monovalent and one trivalent metal cation to replace the position of Pb in the crystal structure, forming so-called ordered double perovskites with a general chemical formula of...
A2B3B′X6. This strategy is very effective because it maintains the 3D perovskite structure and at the same time offers more material diversity. Through combining different A, B+, B‴ and X elements (for example, A = K, Rb, Cs; B‴ = Li, Na, K, Rb, Cs, Ag; B‴ = Al, Ga, In, Sb, Bi, Sc, Y, and X = F, Cl, Br, I), more than 100 double perovskites with a structural tolerance factor and octahedra factor in a reasonable range have been predicted to be thermodynamically stable.\(^\text{[9]}\) Therefore, the structural and functional diversity, combined with the high stability observed in double perovskites, make them very promising lead-free candidates for a wide range of optoelectronic applications.

Of these double perovskites, Cs2AgBiBr6 stands out among the rest, possessing similar optoelectronic properties to lead-based perovskites such as a 3D structure, a long carrier lifetime, a relatively small carrier effective mass, while additionally demonstrating high stability and low toxicity. Indeed, to date, Cs2AgBiBr6 solar cells have delivered improved PCE of over 3%, and Cs2AgBiBr6 single crystals demonstrate high sensitivity to X-ray (detectable dose rate of 59.7 nGyair s\(^{-1}\)).\(^\text{[10,11]}\)

However, despite these favorable characteristics and promising applications, Cs2AgBiBr6 still faces some challenges which require further systematic research. For example, the wide indirect bandgap of Cs2AgBiBr6 largely limits the PCEs of corresponding photovoltaic devices. Moreover, the fundamental structural, optical, and electronic properties of Cs2AgBiBr6 are still not yet fully understood. Therefore, a timely review is needed to identify the characteristics of this emerging material, the current technical challenges that it faces, and its potential for future optoelectronic applications.

This review focuses on the emergence and development of the promising benchmark lead-free double perovskite Cs2AgBiBr6. First, the structure-property relation, synthesis, and stability of Cs2AgBiBr6 are emphasized. Next, the fundamental optical and electronic properties, i.e., the absorption, photoluminescence, electron-phonon coupling, defects, charge carrier dynamics, and bandgap engineering, are discussed. Then, the recent progress in optoelectronic applications including solar cells, photo/X-ray detectors, and ferroelectric/magnetic devices, etc., are reviewed. Finally, the main challenges facing Cs2AgBiBr6 materials and related applications are presented alongside perspectives and possible solutions that may allow for the achievement of commercial, high-efficiency, stable, and nontoxic lead-free optoelectronic devices.

2. Lead-Free Double Perovskite Cs2AgBiBr6: Structure, Synthesis, and Stability

2.1. Structure-Property Relation

2.1.1. Structure and Chemical Bonds

Typical double perovskites implement a heterovalent substitution strategy of using a monovalent and a trivalent metal cation to replace Pb and retain the 3D connectivity of the structure. The crystal structure evolution from standard MAPbI3 to Cs2AgBiBr6 and its derivatives as well as representative band structures are presented in Figure 1. Lead perovskite MAPbI3 (Figure 1a) utilizes a cubic structure (space group Pm3m) at high temperature over 327 K,\(^\text{[12]}\) with the octahedra maintained by I−–Pb–I bond angle of 90° and Pb–I bond length of 3.136 Å.\(^\text{[13]}\) As shown in the inset of Figure 1a the valence band maximum (VBM) of MAPbI3 consists mainly of the antibonding states of Pb s and I p orbitals, and conduction band minimum (CBM) is composed of the antibonding states of Pb p and I s orbitals, which results in the direct bandgap with high absorption. Note that the I orbital is omitted in the schematic.

Cs2AgBiBr6 displays a similar cubic double perovskite structure with a space group of Pm3m (lattice parameter 11.27 Å) at room temperature (RT).\(^\text{[14]}\) This so-called rock salt ordering structure is formed by alternating corner-connected [AgBr6]5− and [BiBr6]3− octahedra in all three directions with Cs+ located at the framework cavities (Figure 1b). The configuration of the octahedra, including the volume variation and distortion/tilting (mainly associated with bond lengths and bond angles), have a significant effect on the electronic structure and thus determine the optoelectronic properties of the perovskites. In ordered Cs2AgBiBr6, the corresponding Ag−Br/Bi−Br and Ag−Br/Bi bonds all maintain a 90° or 180° angle, and the bond length for Ag-Br and Bi-Br is comparable (2.804–2.828 Å). A shorter bond length compared with MAPbI3 means the electrons are more tightly bound to the atoms, contributing to stronger bond strength and stiffness in the Cs2AgBiBr6 framework.\(^\text{[15]}\) Basically, the [AgBr6]5− and [BiBr6]3− octahedra volume are determined by the metal ionic radius (1.15 and 1.03 Å for Ag+ and Bi3+, respectively), the electronegativity (1.93 and 2.02 for Ag+ and Bi3+, respectively) and the interaction from neighboring octahedra, which yield a combined result of complex volume variation such as expansion or contraction of octahedra.\(^\text{[16]}\)

The tilting/distortion of octahedra is partially caused by the mismatch of the octahedral sublattice, and to accommodate this mismatch, strain relaxation will modify the bond lengths/angles. Experimentally, detailed structural information can be obtained from the Raman vibrational modes and refinement of X-ray diffraction (XRD) patterns.

The corresponding band structure of Cs2AgBiBr6 is simplified in inset of Figure 1b revealing that the VBM is composed of Ag d, Bi s character and CBM has Ag s, Bi p character which locate at different positions. Here the Br p orbital that contributes to both VBM and CBM is omitted as well in the schematic. Hence the hybridization between Ag and Bi orbitals at band edges is responsible for the indirect bandgap nature. Although Cs+ orbitals do not make obvious contributions near band edges, they can have an impact on the band structure through bonding interaction between Cs+ and the metal framework. Understanding the structure-property relationship is important to design and achieve Cs2AgBiBr6 based materials with desirable optoelectronic properties. For example, a homogenous octahedral contraction and shrinkage of Bi−Br–Ag bonds in Cs2AgBiBr6 can promote the overlap of elemental orbitals and thus lead to bandgap narrowing.\(^\text{[17]}\) Under thermal treatment, Cs2AgBiBr6 will show a lattice expansion with varied Ag−Br and Bi−Br bond length and the thermal expansion coefficient of Ag−Br bond is obviously larger than the Bi−Br bond, suggesting that variation of the Ag−Br bond is the main contributor to lattice thermal expansion.\(^\text{[18]}\) These anharmonic fluctuations of Ag−Br and Bi−Br bonds change the energy
band structure, which are one of the main factors for the observed thermochromism of Cs$_2$AgBiBr$_6$ crystals and films.\[19\]

2.1.2. Atomic Arrangement

Apart from chemical bond variation, the atomic arrangement in Cs$_2$AgBiBr$_6$ can also significantly affect the band structure and optoelectronic properties.\[20\] Here the metal atomic arrangement is discussed, i.e., the cation order/disorder of Ag and Bi octahedra (Figure 1b,c). Similarly, B$^+/B^{3+}$ alternate cation order also heavily influences the optoelectronic properties especially the magnetic and ferroelectric properties of oxide double perovskites A$_2$B$^+/B^{3+}$O$_6$.\[21\] In a regularly ordered crystal structure, each [AgBr$_6$]$^{5-}$ octahedra is surrounded by six [BiBr$_6$]$^{3-}$ octahedra and vice versa. It should be noted that the solution processing of Cs$_2$AgBiBr$_6$ films or crystals will cause vacancies, interstitials, and antisites including Ag-on-Bi and Bi-on-Ag, leading to lattice disorder.\[10,22\] The ordering degree ($\eta$) of Cs$_2$AgBiBr$_6$ can be described with the following formula:

$$\eta = P_A^x - P_A^0 = P_B^0 - P_B^{4x} = 2x - 1$$

where $P_A^x$ and $P_B^0$ represent the relative occupancies ($x$) of A atoms on A site and B site, respectively.\[21,23,26\] Thus, for a perfectly ordered structure, $\eta = P_A^x = P_B^0 = 1$, while for a completely disordered structure, $P_A^x = P_B^0 = 0.5$, and $\eta = 0$.

Experimentally, the disordered behavior can be observed in the XRD pattern because of the different scattering effects of Ag$^+$ and Bi$^{3+}$ and the reduced symmetry in the disordered structure.\[10\] The degree of the disorder can be simply determined by comparing the peak intensity of oxide super lattice order-related plane (111) and the normal lattice-related reflection plane (022), with a higher ratio representing a higher order extent.\[25,26\] The atomic arrangement in the double perovskite has a big effect on its optoelectronic properties, including bandgaps, lattice distortion, defects, and carrier mobility. By manipulating cations from ordered to disordered, Cs$_2$AgBiBr$_6$ shows enhanced light absorption in the visible and near-infrared region, with the band structure changing from 1.46 eV indirect to 0.44 eV pseudo direct bandgap,\[20\] providing a promising method to improve light absorption of Cs$_2$AgBiBr$_6$. The bandgap narrowing arises from the altering of band hybridization in the reduced crystal symmetry caused by disordered arrangement of [AgBr$_6$]$^{5-}$ and [BiBr$_6$]$^{3-}$ octahedra. Unfortunately, this strategy requires very high temperatures (beyond 1200 K) which greatly limit practical applications. Strategy of using additives such as phenylethylamine bromide (PEABr) can effectively increase the ordering degree because of the selective coordination effect between the functionalized groups in PEA$^+$ and metal framework. Ordered crystals present less lattice distortion, reduced defect density, suppressed trapped-exciton formation, enhanced carrier mobility, hence superior X-ray detection performance.\[25\] For potential optoelectronic applications, disordered antisites are attributed to deep-level defects, which decrease the carrier mobility and cause carrier recombination in Cs$_2$AgBiBr$_6$.\[27\] Therefore, to obtain highly ordered Cs$_2$AgBiBr$_6$, researchers need to pay attention to the key growth factors such as using moderate temperature, slower synthesis speed, higher pressure, suitable additives or dopants in the material fabrication process.\[28,29\]
2.1.3. Layered Structure

To modulate the properties of Cs2AgBiBr6 double perovskite such as a transition from indirect to direct bandgap, or selectively tune the bandgap, layered Cs2AgBiBr6 derivatives have been developed based on specific organic spacer cations, forming homologous compounds with stoichiometries of R4AgBiX8, R2CsAgBiX7, and R2AgBiX8 which adopt the single-layer (n = 1) Ruddlesden-Popper (RP) structure, bilayer (n = 2) RP structure (Figure 1d) and single-layer Dion-Jacobson (DJ) structure (Figure 1e), respectively. However, layered Cs2AgBiBr6 derivatives with a DJ structure (n = 2) or n values greater than 2 for RP and DJ structure have not been demonstrated experimentally so far.

A wide choice of organic cations is available because layered structures do not have a strict restriction on the length or size of the interlayer organic spacer cations. Representative bulky R cations in Cs2AgBiBr6 derivatives are monovalent alkyl-ammonium cations such as propylammonium (PA, CH3(CH2)2NH3+), butylammonium (BA, CH3(CH2)3NH3+), and divalent cations such as 1,4-butanediammonium (BDA, (CH2)4(NH2)2)2+.[30,31] To choose a specific R cation for a potential optoelectronic application, one should consider the interaction between the inorganic framework and the organic cations. Generally, R cations that have smaller interlayer distance and stronger hydrogen bonding, coupled with π–π interactions, would generate higher charge transport efficiency in the layered perovskite. R cations can also be selectively tailored to be highly luminescent or to contribute to perovskite ferroelectricity.[32,33] The incorporation of R cations causes obvious distortion or tilting of the perovskite lattice (related to the Ag-halide-Bi bond and metal-halide bond), crystallizing the lattice in a monoclinic or triclinic system with lower symmetry. Compared with the [BiBr6]6− octahedra, the distortion of [AgBr6]6− octahedra is more pronounced, with a larger deviation in the equatorial and axial Ag–Br bond lengths, arising from the mixing of filled Ag nd orbitals with empty (n+1)s orbitals.[33]

Regarding the properties of low-dimension Cs2AgBiBr6 derivatives, their optical bandgaps are usually larger than their 3D counterparts, with minimal difference between varied R cations, therefore further understanding is needed to explain what contribution the R cation makes to the structure and properties of Cs2AgBiBr6. The indirect bandgap of Cs2AgBiBr6 becomes direct in most cases when the inorganic framework becomes a monolayer, with the typical band structure shown in the inset of Figure 1e. This direct transition originates from the single-metal-organical contributions to the VBM and CBM of layered Cs2AgBiBr6 derivatives in the case of n = 1. This dimension reduction would result in more pronounced lattice distortion and reshaping the orbital composition of the band edges.

Given that the corresponding photoluminescence is usually too weak to be observed at RT and the more distorted structure, layered Cs2AgBiBr6 perovskite derivatives presently appear to have limited optoelectronic applications. However, these low dimensional perovskites offer a research platform for self-trapping emission arising from electron-phonon coupling, or ferroelectric, ferro/antiferromagnetic, and spin-electronic applications.

2.2. Synthesis and Stability

The synthesis processes of Cs2AgBiBr6 materials such as single crystals, thin films, nanocrystals, and quantum dots are facile and simple. Approaches including cooling-induced crystallization, inverse temperature crystallization, antisolvent vapor crystallization and slow solvent evaporation have been widely used to grow bulk perovskite single crystals. One-step solution deposition (spin-casting or spray-coating) methods can be used to deposit high-quality Cs2AgBiBr6 films if one carefully controls the precursor stoichiometry.[34] In contrast, vacuum-evaporation deposited Cs2AgBiBr6 thin films usually suffer from halogen losses, which may introduce additional point defects. Cs2AgBiBr6 nanocrystals and quantum dots with uniform shape, high purity and high crystallinity have been synthesized using hot-injection and ligand-assisted reprecipitation methods.[35,36] These nanoscale materials hold potential for lighting applications due to the strong quantum confinement effects. Detailed synthesis methods and related discussions can be found in a recent article by Yang et al.[37] The synthesis should be carried out bearing in mind that the properties of Cs2AgBiBr6 including the stoichiometry, atomic arrangement, chemical bond, energy level, crystallinity, conductivity, and mobility, etc., depend on the specific fabrication method.

One of the most attractive properties of Cs2AgBiBr6 is its superior stability compared with lead-based materials. All inorganic Cs2AgBiBr6 shows excellent moisture, light, and thermal stability. Crystals show no signs of decomposition for up to 240 days in ambient atmosphere, with even the chemical bonds remaining unchanged.[38] Also, no evidence of decomposition is detected for crystals irradiated (halogen lamp, 0.75 sun) at 50 °C for 30 days, or heated at 100 °C for 72 h and mass loss is only observed at temperatures higher than 430 °C.[39] As a quaternary compound, Cs2AgBiBr6 can form a single-phase without any competing binary or ternary phases, proved by both phase thermodynamic stability diagram evaluation and experimental results. While Cs2AgBiBr6 usually crystallizes in a space group of Fm3m with a face-centered-cubic structure at RT, phase transitions (cubic, tetragonal, monoclinic, and triclinic) may occur when one decreases the temperature, modulates the material dimensions, uses high pressure treatment, or incorporates new elements into the lattice. For instance, the room temperature cubic phase (space group Fm3m) will transform to a tetragonal phase (space group I4/m) at 122 K or high pressure of ~2.3 GPa.[40,41] A similar phase transition has been observed when a certain amount of Fe replaces the Bi position in the lattice, causing reduced symmetry in the octahedra.[42] To estimate the structural stability of ARX4 perovskites, the Goldschmidt tolerance factor and the octahedral factor have been proposed. The tolerance factor τ with high prediction accuracy and octahedral factor μ is defined as:

\[ \tau = \frac{r_A}{r_B} - n_e \left( \frac{r_A}{r_B} - \frac{r_A}{r_B} \right) \ln \left( \frac{r_A}{r_B} \right) \]

\[ \mu = \frac{r_A}{r_B} \]

where \( r_i \) is the ionic radius of ion \( i \), \( n_e \) is the oxidation state and \( r_A > r_B \) by definition. Stable perovskite forms when \( \tau < 4.18 \) and

\[ \mu > 0.8 \]
0.44 ≤ μ ≤ 0.9. For double perovskite like Cs2AgBiX6 (X = Cl or Br), rB is approximately calculated to be the average of the Ag+ and Bi3+ radius and thus the (μ, τ) is in the stable ranges of (0.56–0.60, 4.07–4.21). Moreover, the decomposition energies (ΔH) with respect to possible decomposition pathways including CsBr, AgBr, Cs2AgBr3, CsAgBr2, and Cs3Bi2Br9 are calculated to be positive and larger than that of MAPbI3, suggesting a higher thermodynamic stability of Cs2AgBiBr6.[44] Note that ΔH of the closely related Cs2AgBiI6 is negative, indicating Cs2AgBiI6 is unstable and may decompose spontaneously.[27] These methods are useful to predict the probability of successfully synthesizing novel Cs2AgBiBr6-based perovskites by engineering the A, B, or X sites using new elements.

The intrinsic high stability of all-inorganic Cs2AgBiBr6 tends to guarantee the high stability of its optoelectronic devices. Taking a solar cell as an example, unencapsulated Cs2AgBiBr6 solar cells show no obvious PCE degradation for more than 4 months (hole transport layer (HTL) free, temperature: 20–30 °C, humidity: 40–60%).[45] However, for practical devices using organic interlayers, stability issues appear because of the instability of organic materials and interfaces. When stored at higher humidity (68±7%) for 68 days, unusual ion migration of Ag and Br from Cs2AgBiBr6 to P3HT/Cu interface is detected in solar cells, possibly caused by the volatility of halide and/or reactivity of halide with Ag or Cu metals.[46] Indeed, there are some discrepancies in different studies about the ambient stability of solar cells using P3HT or Spiro-OMeTAD HTL.[46,47] Therefore, further investigation is still needed to point out the potential degradation pathways for Cs2AgBiBr6 optoelectronic devices using organic interlayers under various testing conditions, such as continuous light-illumination, to guarantee a high stability for practical applications.

3. Fundamental Optoelectronic Properties of Cs2AgBiBr6

3.1. Photophysics of Absorption and Photoluminescence

As an indirect bandgap semiconductor, Cs2AgBiBr6 shows a moderate absorption coefficient of around 4 × 10^4 cm–1 at energies higher than 2.5 eV.[48] As a comparison, MAPbI3 has a large absorption coefficient in the order of 10^5 cm–1 over almost the whole visible range.[49] For the typical absorption spectrum of Cs2AgBiBr6 films, as shown in Figure 2a, we usually observe three regions. At lower wavelengths, we observe a flat and high absorption range, which is attributed to the direct bandgap absorption. A characteristic and strong peak located at around 438 nm is observed and questions remain about the origin of this peak.[50] This sharp peak, which contributes more than 20% of the overall light absorption of Cs2AgBiBr6 perovskite, has been assigned to either excitonic absorption, the charge-transfer-like transition between Ag and Bi/Br orbitals, or localized Bi 6s-6p transitions. Recently, this characteristic absorption peak has been observed in Cs2AgBiBr6 solar cells and attributed to the charge-transfer-like transition between Ag and Bi/Br orbitals.[46] Indeed, there are some discrepancies in different studies about the ambient stability of solar cells using P3HT or Spiro-OMeTAD HTL.[46,47] Therefore, further investigation is still needed to point out the potential degradation pathways for Cs2AgBiBr6 optoelectronic devices using organic interlayers under various testing conditions, such as continuous light-illumination, to guarantee a high stability for practical applications.

![Figure 2.](image-url)

Figure 2. a) Typical absorption spectrum of Cs2AgBiBr6 films with the inset showing the absorption onset at 610 nm. Reproduced with permission.[45] Copyright 2017, WILEY-VCH GmbH & Co. KGaA, Weinheim. b) Plot of the center of absorption peak versus smallest side length of cubes of Cs2AgBiBr6 NCs. Inset shows graphs of a suspension of Cs2AgBiBr6 NCs and the orange-red bulk material. Reproduced with permission.[45] Copyright 2018, American Chemical Society. c) PL spectrum of Cs2AgBiBr6 powders fitted using a Gaussian function. Red: fit peak 1, green: fit peak 2, blue dashed line: cumulative fit peak. Reproduced with permission.[55] Copyright 2017, WILEY-VCH GmbH & Co. KGaA, Weinheim. d) Fluence-dependent PL decays of Cs2AgBiBr6 SC upon 530-nm laser excitation. Reproduced with permission.[57] Copyright 2021, American Association for the Advancement of Science. e) The absorbance (black), high-energy PL spectrum (red), and PLE spectrum (blue) recorded at emission energy of 2.0 eV at room temperature. Inset: high-energy PL spectrum (red) and PLE spectrum (blue) of the same sample at 8 K. Reproduced with permission.[52] Copyright 2020, American Chemical Society.
peak has been demonstrated to show no strong dependence on Cs$_2$AgBiBr$_6$ nanocrystal sizes, as shown in Figure 2b, reflecting that the peak does not in fact originate from confined excitons.[33] Furthermore, the photo-emissions related to this absorption peak are virtually independent of sample temperature, which contrasts with exciton emission behavior, as exciton emission normally shifts with temperature.[52] Therefore, the possibility of excitonic absorption should be excluded based on these findings. However, regarding the transition between the Ag 4d and Br/Bi p orbitals, the possibility of this transition-induced absorption cannot be fully excluded, because it exhibits similar energy with Bi 6s-6p orbital transition. Note that a similar peak also appears in the absorption spectrum of Bi-based halide material such as Cs$_3$Bi$_2$Br$_9$.[53] so we tend to attribute the nature of the peak to the s-p transition of bismuth in [BiBr$_6$]$^{3–}$ octahedra. Specifically, this absorption is related to an optical transition from $^1$S$_0$ ground state to the triplet $^3$P$_1$ excited state of Bi$^{3+}$ in Cs$_2$AgBiBr$_6$. Even though the transition is spin forbidden, the transition is allowed because of the strong spin-orbit coupling of heavy Bi$^{3+}$.[52] A weak and broad tailing absorption at higher wavelength is also observed (with an edge at ≈610 nm), which originates from the indirect bandgap absorption. An estimate of the exciton binding energy of Cs$_2$AgBiBr$_6$ could be obtained from the absorption edge at the direct transition using the Elliott model, providing a high exciton binding energy of 268 meV.[54]

The photoluminescence (PL) of Cs$_2$AgBiBr$_6$ at RT is relatively weak, broad, and shows a Stokes shift, which is believed to be caused by the indirect bandgap and the electron-phonon coupling. The electron-phonon coupling will be discussed in the following section. The origin of the emission of Cs$_2$AgBiBr$_6$ remains a subject under debate. Cs$_2$AgBiBr$_6$ usually shows a broad red emission (at RT) situated at 600–700 nm, which reveals two PL peaks through Gaussian fitting of the broad PL spectrum (Figure 2c) with the higher energy peaks assigned to band edge emission from the indirect bandgap and the other lower energy emission attributed to the defect states in band structure or self-trapped excitons (STEs).[38,52,55] Note that there are reports claiming that the PL peak results from the spatially localized color centers which can be either intrinsic self-trapping of excitons/carriers or defects.[50,56] Instead, we have recently demonstrated that the PL emission of Cs$_2$AgBiBr$_6$ is mainly from the band-to-band emission. To start, the fluorescence-dependent PL intensity versus carrier density is measured and reveals a power-law factor of 1.94 and 1.26 when the excitation density is smaller or larger than 10$^{16}$ cm$^{-3}$, respectively, which implies both free carrier and exciton emission in Cs$_2$AgBiBr$_6$ samples. The PL decay dynamic is then compared and shows a photoexcitation fluence-dependent behavior (Figure 2d), suggesting that the PL is from free carrier band-to-band emission because the defects or exciton emission rate is typically independent of the excitation density in the low regime. We speculate that the emission contribution from defects or STEs is small considering the single-peak and fluorescence-dependent PL emission behavior. The fitting of the decay curves using an expression of $dn/dt = -k_1n - k_2n^2$, where $k_1$ and $k_2$ are the first-order Shockley-Read-Hall recombination and second-order electron-hole (bimolecular) recombination coefficients respectively, yields a relatively larger $k_2$ of 4.5 ± 0.1 × 10$^{-11}$ cm$^3$ s$^{-1}$ than traditional indirect semiconductors such as Si or GaP (10$^{-13}$ to 10$^{-14}$ cm$^3$ s$^{-1}$). The nature of the emission is actually a polaronic band-to-band transition, meaning the emission is accompanied by the lattice deformation and this also explains the breaking of forbidden transition rules.[57]

Apart from the red emission, interestingly, a high energy blue emission at 2.825 eV is also detected with significantly lower peak intensity, as shown in Figure 2e. The split photoluminescence excitation (PLE) spectra recorded at the conventional red emission reveal two features located ≈50–60 meV above/below the absorption peak, which suggests a carrier cooling process from at least two excited states close to the absorption peak down to the luminescent state (red emissive). A reduced PLE signal at the absorption peak position is observed (more obvious at low temperature), correlating well with the emergence of blue emission. The origin of this blue emission is attributed to the carrier transition between the $^1$S$_0$ ground state and the $^3$P$_1$ triplet state of [BiBr$_6$]$^{3–}$ complex which also leads to the strong absorption peak. The radiative lifetimes of the excited state from the dominant transition are very short (about 30 ps) and thus result in a very weak blue PL emission and simultaneously enable a relaxation to the ground state (red emission).[52]

Note that for experimentally measured PL emission, the variations in fabrication (solution process or vacuum deposition, etc.) and post treatment methods (annealing or high pressure, etc.) contribute to different stoichiometry, atomic arrangement, dimensionality, morphology, crystallinity, electronic structure, and defect distribution in Cs$_2$AgBiBr$_6$ samples, which cause the PL spectrum discrepancies. Another important point is to improve the PL performance of Cs$_2$AgBiBr$_6$ as it is highly related to optoelectronic applications. Promising methods are to optimize the material quality so as to reduce the non-radiative defects, change the bandgap from indirect to direct type, decrease the electron-phonon coupling (for instance, emission of Cs$_2$AgBiBr$_6$ can be highly bright at cryogenic temperature) or introduce emissive dopants such as lanthanide doping of Eu or Yb.[58]

It is still challenging to obtain direct-bandgap Cs$_2$AgBiBr$_6$ with high intrinsic PL performance currently, the reported direct-bandgap Cs$_2$AgBiBr$_6$ and its derivatives have shown either lower PL or a complete lack of PL performance. For example, the dilute Tl-doped Cs$_2$AgBiBr$_6$ is direct bandgap but shows no PL performance, which might be caused by the symmetry-forbidden bandgap transition.[59,60] Future improvement is expected to break the forbidden transition through band structure engineering.[61] Cs$_2$AgBiBr$_6$ derivatives such as layered perovskite (BA)$_3$AgBiBr$_6$ display weak and slightly broadened PL even at 20 K, and quench rapidly upon warming. We speculate that it is because the dimensional reduction has led to significantly distorted lattice and introduced more non-radiative defects.[31] Therefore, further investigation is required to realize high PL emission in Cs$_2$AgBiBr$_6$ and its derivatives at RT.

### 3.2. Giant Electron-Phonon Coupling

In a real crystal lattice, atoms are not fixed but are vibrating all the time at RT. Phonons, defined as the quantum of lattice vibration, are classified as optical phonon and acoustic phonon...
branches. In the former mode, the atoms in the unit cell show out-of-phase displacement whereas in the latter mode the atoms have an in-phase vibration. It is generally recognized that the carrier-phonon scattering, especially the electron-optical phonon coupling, is a fundamental interaction effect that plays a major role in determining the charge carrier mobility and excitation-emission of perovskites. Likewise, the acoustic phonon interactions determine the thermal properties of a material. Usually, for perovskites, a strong electron-phonon coupling would result in obvious carrier scattering and decrease the carrier mobility. Furthermore, it also leads to a large Stokes shift and broadens the PL line widths. A study on the electron-phonon coupling mechanism is therefore important to describe the charge carrier dynamics and fully understand the fundamental optoelectronic properties of perovskites. For traditional lead-based perovskites such as MAPbX₃ or FAPbX₃, the Frohlich coupling between carriers and longitudinal optical (LO) phonons rather than the acoustic phonon deformation potential coupling or scattering from ionized impurities, is demonstrated to be the dominant charge carrier scattering mechanism at RT.²⁶,²⁷

For Cs₂AgBiBr₆ double perovskite, the scattering becomes more complicated because of the complex environment caused by additional B-site metal vibrations. Using a combination of optical spectroscopic techniques and density functional theory (DFT) calculations, a giant electron-phonon coupling in Cs₂AgBiBr₆ was observed.²⁸ As shown in Figure 3a, the typical PL emission peak narrows as the temperature decreases. The dependence of the PL linewidth on temperature can be compactly expressed as:

\[
\Gamma(T) = \Gamma_0 + \Gamma_{ac} + \Gamma_{LO} = \Gamma_0 + \gamma_{ac}T + \gamma_{LO}n(T)
\]

where \(\Gamma_0\) is a constant and represents the inhomogeneous broadening parameter arising from the scattering from the disorder or imperfections.²⁵,²⁶ The second and third terms \(\Gamma_{ac}\) and \(\Gamma_{LO}\) are temperature-dependent parameters, representing the scattering from acoustic phonons and LO phonons with electron-phonon coupling strengths of \(\gamma_{ac}\) and \(\gamma_{LO}\), respectively. \(n(T)\) is the population of electron-LO phonon coupling, as given by Bose-Einstein distribution \(n(T) = 1/(\exp(h\omega/k_B T) - 1)\), where

---

**Figure 3.** a) Temperature dependence of Cs₂AgBiBr₆ emission line width. The FWHM of single-crystal Cs₂AgBiBr₆ steady-state PL spectra as a function of temperature, with an example of measured raw PL data provided in the inset for several different temperatures. The red line is a fit made with Equation (4) while the acoustic and LO phonon coupling are parsed via the blue and green traces, respectively. b) Raman spectrum of Cs₂AgBiBr₆ recorded using 808 nm excitation, revealing the T₂g mode of Cs⁺ ions at 40 cm⁻¹, the T₂g (breathing), E₂g and A¹g (both stretching) modes of the [AgBr₆]⁻ octahedron at 75, 135, and 175 cm⁻¹, respectively. The inset shows a representation of the primitive cell. a,b) Reproduced with permission.²⁸ Copyright 2018, American Chemical Society. c) Temperature-dependent PL linewidth of Cs₂AgBiBr₆ SC. The dashed line is fitted with the conventional Equation (4) and the solid line is fitted with the model proposed by Toyozawa et al. for strong coupling. d) The TR kinetics of Cs₂AgBiBr₆ SC probed at 440 nm. e) Schematic of the self-trapping of charge carriers by acoustic phonons. The dots between adjacent perovskite octahedra represent the omitted lattice units for simplicity. f) Schematic of the energy diagram for carrier self-trapping under the generalized coordinate. c–f) Reproduced with permission.²⁷ Copyright 2021, American Association for the Advancement of Science.
\(\Delta E_{\text{stokes}} = 2\hbar \omega\)  \hspace{1cm} (5)

\[
\text{FWHM} = 2.36 \sqrt{\frac{\Delta E_{\text{stokes}}}{\hbar \omega}} \cosh \left( \frac{\hbar \omega}{2k_B T} \right)
\]  \hspace{1cm} (6)

where the Stokes shift energy \(\Delta E_{\text{stokes}}\) is obtained from the PL and absorption spectrum of Cs\(_2\)AgBiBr\(_6\) and FWHM is the full width at half maximum values of PL peaks at different temperatures. A small \(S < 1\) generally indicates weak electron-phonon coupling and carrier localization. While for Cs\(_2\)AgBiBr\(_6\), the reported \(S\) value is relatively large, reaching between 11 and 16.\(^{16,64}\) Combined with DFT results, the Fröhlich phonon coupling constant \(\alpha\) can also be calculated by the following formula:\(^{71}\)

\[
\alpha = \frac{e^2}{\hbar \omega} \frac{1}{4\pi \varepsilon_0} \sqrt{\frac{\epsilon^* - 1}{2\hbar \omega (\epsilon - \varepsilon_s)}}
\]  \hspace{1cm} (7)

where \(e\) is the electric unit, \(\varepsilon_0\) is the vacuum permittivity, \(\epsilon^*\) is the effective mass and \(\epsilon_0\) and \(\epsilon_s\) are the electronic and static dielectric constants, respectively. Note that the calculated Fröhlich coupling parameter of Cs\(_2\)AgBiBr\(_6\) is comparable with that of lead-based perovskite (\(\alpha = 2\)),\(^{71}\) which is notably lower than experimental results. It is reasonable because the simulated calculation uses a perfect ordered structure, which would underestimate the coupling constant.

Moreover, through Raman spectrum characterization, one can obtain useful lattice dynamics information revealing the contribution of the vibrations from [AgBr\(_6\)]\(^{5-}\) or [BiBr\(_6\)]\(^{3-}\) sublattice. Representative Raman spectra recorded using 808 nm excitation in Figure 3b reveal a low-energy vibration of Cs\(^+\) ions with translational mode and three higher energy modes corresponding to a single breathing and two stretching vibrations arising from [AgBr\(_6\)]\(^{5-}\) sublattice where we can identify the LO phonon (A\(_{1g}\) symmetry) energy. However, currently there is a disparity about the origin of the Raman peak, especially the main A\(_{1g}\) peak, possibly because the assignment is related to specific DFT calculation.\(^{19,56,64}\) Further investigation is therefore needed to clarify the main vibration origins of the Cs\(_2\)AgBiBr\(_6\) lattice.

Very recently, evidence of strong deformation potential (defined as the derivative of the electronic energy levels due to the phonon scattering) has been uncovered in Cs\(_2\)AgBiBr\(_6\) through systematic spectroscopy measurements and DFT calculations.\(^{57}\) By investigating the temperature-dependent PL bandwidth broadening (Figure 3c), it is found the typical expression of \(\Gamma(T)\) as discussed before is not valid for the PL bandwidth at high temperatures (\(\sim\)200–300 K). Instead, the temperature-dependent PL linewidth shows a proportional correlation to the square of the temperature \(\sqrt{T}\), providing solid evidence of strong electron-phonon coupling in Cs\(_2\)AgBiBr\(_6\).\(^{72}\) Note that the discrepancies are observed between different reports and the fitting may bear some uncertainties due to limited data points and too many variables. The Fröhlich coupling constant \(\alpha\) is then calculated to be 2.68 and 2.52 for electrons and holes, respectively, suggesting an intermediate Fröhlich coupling. In sharp contrast, the deformation potential is 13.7 and 14.7 eV at VBM and CBM of Cs\(_2\)AgBiBr\(_6\), which is greatly improved compared with lead-based perovskite such as CsPbBr\(_3\) (2.2 and 6.3 eV). We therefore believe that the optical phonons (Frohlich coupling) and acoustic phonons (deformation potential) both synergistically contribute to the electron-phonon scattering mechanism and the PL linewidth broadening. The broadening contribution differs at varied temperature, revealing that at higher temperature the acoustic phonon scattering is stronger than optical branches and at low temperature the optical phonons scattering dominates. Ultrafast transient reflection (TR) dynamic (Figure 3d) analysis reveals a fast scattering and trapping process, with \(t_1\) attributed to hot carrier relaxation via LO phonons and formation of Fröhlich polaron and \(t_2\) (about 4 ps) assigned to the electron-acoustic phonon coupling and ultrafast self-trapping of the carriers by the acoustic phonons. The assignment is reasonable considering \(t_1\) and \(t_2\) are intrinsic parameters for Cs\(_2\)AgBiBr\(_6\) because they are invariant to the defect density and excitation concentrations. Thus, the self-trapping process can be understood as shown in Figure 3e,f. The electron and hole charge carriers in Cs\(_2\)AgBiBr\(_6\) are first localized by optical phonons (with a time constant of 0.2 ps) and then are self-trapped by acoustic phonons (with a time constant of around 4 ps), which further localize the charge carriers.

As discussed previously, the giant electron-phonon coupling including both optical and acoustic branches in Cs\(_2\)AgBiBr\(_6\) typically introduces more carrier scattering, limits the carrier mobility, and decreases the color purity of light emitters. Therefore, it is expected that finely modulating this scattering effect will solve these intrinsic limitations of Cs\(_2\)AgBiBr\(_6\) for efficient optoelectronic devices such as solar cells, detectors, and LEDs. Furthermore, increasing the lattice order degree, maintaining a highly symmetric cubic structure, introducing chemical/mechanical pressure, and engineering the elemental composition are promising strategies for tuning the electron-phonon coupling strength in Cs\(_2\)AgBiBr\(_6\). Controlling the electron-phonon coupling may be of particular interest as in some cases giant coupling in perovskite can be used to produce THz radiation or white emission.\(^{31}\)

### 3.3. Defects: Tolerant or Not?

Ideally, in a semiconductor crystal lattice, all the atoms reside at their specific positions without any defects or impurities. However, in real cases, lots of defects are inevitably generated...
during the growth and processing of materials. Defects in semiconductors are mainly classified into point defects (i.e., vacancies, interstitials, and antisites), line defects (i.e., dislocation), plane defects (i.e., surface and grain boundaries), and bulk defects (i.e., voids or precipitates). Defects significantly affect the charge carrier transport/recombination dynamics in perovskite materials and devices, therefore understanding defects at a fundamental level is important for achieving highly efficient optoelectronic devices. Lead-based perovskite is highly defect-tolerant because most of the formed defects are found to be shallow level defects (states appear closely above the VBM or below the CBM) which barely affect the materials optoelectronic properties such as the charge carrier mobility and lifetime. The high defect tolerance of lead-based perovskite is attributed to its strong antibonding coupling between Pb lone-pair s orbitals, symmetry, high ionicity, and large lattice constant.

In contrast, Cs$_2$AgBiBr$_6$, with its two B-site metals, expresses a very different landscape for defects. Figure 4a,b compares the formation enthalpy of typical point defects in Cs$_2$AgBiBr$_6$ under representative Br-poor and Br-rich conditions, respectively, while Figure 4c,d summarize the thermodynamic transition energy level of different point defects in Cs$_2$AgBiBr$_6$ perovskite. The results are determined by DFT calculation using Heyd-Scuseria-Ernzerh (HSE) hybrid function with the inclusion of spin-orbital coupling (SOC) based on Perdew-Burke-Ernzerhof (PBE) optimized structures.

Twenty different point defects, including vacancies, cation-on-anion antisites, anion-on-cation antisites, and interstitials are studied. We can thus determine from these calculations of Cs$_2$AgBiBr$_6$ that: i) Ag vacancies are the most easily formed defects due to the lowest formation enthalpy, even in Ag-rich conditions.

They are shallow acceptor defects that lead to the intrinsic p-type conductivity and therefore do not deteriorate optoelectronic performance; ii) the dominant deep-level (i.e., located within the middle third of the forbidden bandgap) acceptor defects present low formation enthalpy or energy. These deep defects, which might be Ag$_{Bi}$ antisites, Bi vacancies, Bi$_{Ag}$ antisites, and Br vacancies, are not thermally ionized within the lattice and form uncontrollable non-radiative recombination channels (governed Shockley-Read-Hall recombination), which then eliminate the charges and deteriorate device performance.

iii) Cs$_2$AgBiBr$_6$ thus shows defect intolerance, possessing more deep-level defects compared to lead-based perovskites. However, this does not mean that Cs$_2$AgBiBr$_6$ has more trap-state densities. In fact, it only possesses moderate trap densities (crystal: $1.7 \times 10^9$ cm$^{-3}$; film or device: $10^{16}$–$10^{17}$ cm$^{-3}$).

Apart from these point defects, higher dimensional surface or grain boundary traps are often composed of deep-level defects.

To suppress the unfavorable deep-level defects in Cs$_2$AgBiBr$_6$, it is suggested that the growth condition should be carefully controlled. Note that the formation energy and defect types are very sensitive to the chemical environment or calculation methods, somewhat explaining the disputes in literature.

For instance, questions regarding whether Br and Bi vacancies belong to deep or shallow traps are still under debate. Experimentally, vacuum-deposited Cs$_2$AgBiBr$_6$ films usually show a Br deficient composition and generate inferior photovoltaic performance compared with solution-processed films with a better stoichiometry. Whether post-annealing of the films in Br vapor will improve film quality still waits to be validated. Additionally, reports have noticed using a precursor mixed with excess AgBr and a BiBr$_3$ deficiency may result in increased crystallinity, charge carrier mobility, and carrier lifetimes. However, the formation of an undesired secondary phase is also observed and its impact is not yet elucidated. Hence, in addition to the electronic structure calculations, further experimental characterization (such as capacitance property and deep-level transient spectroscopy) or device performance investigations is imperatively required. Such studies would determine the defect levels and concentrations, explain the relationship between stoichiometry and defects and provide guidance of reducing the deep-level defects in Cs$_2$AgBiBr$_6$.

### 3.4. Charge-Carrier Dynamics

Understanding the charge carrier dynamics of Cs$_2$AgBiBr$_6$ such as the charge carrier generation, relaxation, and diffusion...
process is vital to achieve high-performance optoelectronic devices. For solar cells, photodetectors, and LEDs, it is necessary to gently control these carriers to either separate, deliver photovoltage/photocurrent, or recombine to emit light.

Charge carrier generation in perovskites usually is a very fast process (picosecond), supported by time-resolved terahertz spectroscopy (TRTS). Charge carrier relaxation process in Cs$_2$AgBiBr$_6$ can be studied through femtosecond transient absorption (TA) spectroscopy and time-resolved microwave conductivity (TRMC) measurements. Figure 5a shows the pseudo color TA spectrum of Cs$_2$AgBiBr$_6$ nanocrystals at 350 nm pump with a fluence of $1 \times 10^{15}$ photos/pulse cm$^{-2}$. A ground-state bleaching (GSB) peak at 443 nm is detected, which is caused by the state-filling effect from both the conduction band and the valence band. Another broad photo-induced absorption (PIA) band centered at 520 nm is also observed. When the decay time between the probe and pump shifts from 0.1 to 0.6 ps, the PIA band decreases as the GSB signal increases (Figure 5b), suggesting a typical hot carrier relaxation process of the PIA signal. PIA band is totally replaced by a bleaching band at longer times such as 1 ns. Indeed, analysis of PIA and GSB decay dynamics probed at varied pump fluences reveal the lifetimes for different dynamic processes in Cs$_2$AgBiBr$_6$ nanocrystals (Figure 5c). Note that the build-up dynamics of the GSB band should correspond to the PIA decay dynamics. Thus, the GSB signal presents a fast time constant of 0.2 ps (relaxation of hot holes) followed by a partial decay with a lifetime of 1.4 ps (hole trapping by sub-bandgap states), while the PIA band signal reveals a fast decay of 0.8 ps (relaxation of hot electrons) and a slower decay lifetime of 40 ps (electron trapping by sub-bandgap states). The trapping component by sub-bandgap states can be greatly reduced by a surface passivation agent such as oleic acid (OA), as demonstrated by TA decay. Further extending the decay time of the bleaching signal would provide the signal from long-lived (a time scale of nanoseconds) bimolecular carrier recombination. Moreover, the intrinsic self-trapping of carriers must be considered because of the giant electron-phonon coupling as described above. This self-trapping process is also ultrafast (1–2 ps or less).

TRMC spectra further probe the formation and decay of mobile/free charge carriers in Cs$_2$AgBiBr$_6$. TRMC results are expressed as $\Delta P/P$ (where $P$ is the power of absorbed microwave) as a function of time, normalized for $I_0$ (number of incident photos) and for the surface area of the sample ($A$), which is proportional to the concentration of charge carriers and the sum of their mobility. Upon pulsed irradiation at 580 nm (penetration depth over 5 μm), Cs$_2$AgBiBr$_6$ crystals show a rapid initial decay and a slow long-lived tail in all the pulse-radiolysis TRMC traces, as shown in Figure 5d,e. This fast decay is attributed to surface-related recombination (within hundreds of nanometers of the surface) and the slow decay arises from the mobile charges in the deep bulk of the crystals which could escape from surface recombination. The signals all fall into a timescale of several μs magnitude, implying the presence of mobile charge carriers with long lifetimes comparable with MAPbI$_3$ crystals. At higher temperatures (348 K), increasing

![Figure 5. TA spectra of colloidal OA-capped Cs$_2$AgBiBr$_6$ NCs. a) Pseudo color TA plot pumped with 350 nm. b) TA spectra at indicated delay time from 0.1 ps to 1 ns (350 nm pump with a fluence of $1 \times 10^{15}$ photos/pulse cm$^{-2}$). c) PIA (top) and GSB (bottom) decay dynamics at early time probed at 520 nm (350 nm pump with a lower fluence of $1 \times 10^{14}$ photos/pulse cm$^{-2}$). Reproduced with permission. Copyright 2018, WILEY-VCH GmbH & Co. KGaA, Weinheim. TRMC traces recorded at different photon fluences for Cs$_2$AgBiBr$_6$ NCs upon pulsed laser excitation ($\lambda = 580$ nm) at d) 348 K and e) 198 K. Reproduced with permission. Copyright 2018, American Chemical Society. f) Schematic representation of the charge carrier dynamics of Cs$_2$AgBiBr$_6$. $E_{g}$ means indirect bandgap and $E_{gd}$ means direct bandgap.](image-url)
the photo fluence results in a decreased TRMC signal, indicating a typical high-order recombination process, i.e., bimolecular band-to-band recombination or Auger recombination (Figure 5d). In contrast, it reveals an opposite intensity dependence at lower temperatures (198 K, Figure 5e), which is a signature of charge trapping. This means at low fluence, all the charges are captured by trap states and additional mobile charges will be produced after the saturation of these traps either at high fluence or being thermally released at high temperatures. This also explains the suppression of long-lived tails at 198 K compared with 348 K, caused by the immobilization of charges in shallow trap states, as the photogeneration is independent of temperature and the mobility increases upon cooling. Therefore, the charge carrier dynamics differ at varied temperatures and positions in the crystals. For crystals, the charge lifetime is long enough, in a time scale of microseconds, but for Cs₂AgBiBr₆ thin films (thickness of 150 nm), the long-lived TRMC tails disappear, suggesting surface-related recombination. Reducing surface traps and improving film quality can thus also realize long lifetimes, such as 1.4 μs, in Cs₂AgBiBr₆ films.[48]

To better clarify the charge carrier dynamics, we present a general model of Cs₂AgBiBr₆ dynamics in Figure 5f showing the typical charge carrier generation and recombination process (radiative and non-radiative) together with the time constants. Process I represents the absorption and generation of free carriers or excitons, followed by the hot carrier relaxation to the conduction band minimum. A very weak blue emission is detected with short lifetimes (Process II). The charge carriers or excitons will be trapped/localized by the optical and acoustic phonons and a band-to-band emission (free electron–hole recombination) is observed with the contribution from the phonons (Process III). Process IV presents the trapping and thermal releasing process of charge carriers by the shallow electron/hole traps in the Cs₂AgBiBr₆ materials. This may also involve the radiative recombination process (Process V). For simplicity, Process V can also represent the STE emission. Note that the recombination of Process II, III, and V would well explain the experimentally observed PL spectra of Cs₂AgBiBr₆. At the same time, we would observe competing non-radiative recombination at deep-level bandgap defects and surface/interface traps (Process VI).

The carrier diffusion length (l₀) and carrier mobility of Cs₂AgBiBr₆ are also important properties determining optoelectronic device performance. They are calculated by equations of l₀ = √Dτ and μ = De/(k_BT), respectively, where D is the carrier diffusion coefficient (obtained from cross-sectional time-dependent PL image), τ is the lifetime of the excited carrier, k_B is Boltzmann’s constant, e is the electronic charge, and T is the temperature. By using TRPL lifetime values, the l₀ of Cs₂AgBiBr₆ single crystal is calculated to be from 700 nm to 2.44 μm within the temperature range of RT to 123 K, and the corresponding carrier mobility is 0.8 and 10 cm² V⁻¹ s⁻¹, respectively.[83] The thin films also have the mobility of up to 0.39 (vacuum-processed) and 0.74 (solution-processed) cm² V⁻¹ s⁻¹.[84] For Cs₂AgBiBr₆ films, the carrier diffusion length is up to 110 ± 20 nm for electrons and holes, respectively.[80] Therefore, the long carrier lifetime, long carrier diffusion length, and high mobility make Cs₂AgBiBr₆ an ideal candidate for multiple optoelectronic applications. To further increase the carrier diffusion length in thin films, the carrier lifetime and carrier mobility should be carefully optimized. Traps/defects in films should be largely reduced because they are regarded as trapping sites for carrier recombination. Detailed methods such as employing surface passivators, modifying film morphologies (less grain boundaries), reducing the carrier scattering, and optimizing the device architecture would effectively enable a longer diffusion length in future investigations.

3.5. Bandgap Engineering

Bandgap engineering is an important approach to modulate the optoelectronic properties of semiconductors for potential applications. For Cs₂AgBiBr₆ with a large and indirect bandgap, the engineering strategy mainly includes element doping/ alloying, dimensional reduction, and tuning the order parameter. Doping and alloying are the most powerful methods in tailoring the optical, electrical, and structural properties of semiconductors. By intentional incorporation of elements on A, B or X sites, the properties of Cs₂AgBiBr₆ can be significantly modified. For instance, alkali-metal cations, i.e., lithium (Li⁺), sodium (Na⁺), potassium (K⁺) and rubidium (Rb⁺) have been used to substitute A-site Cs⁺ in Cs₂AgBiBr₆. The substitution ratio should be restricted to a moderate level (e.g., <15%) to avoid the formation of impurities (AₓBₓX₉ phase).[96] These alloying usually result in similar or slightly reduced bandgaps, but they also possess some other altered properties. Specifically, Rb⁺ substitution has exhibited a substantial increase in the X-ray response of Cs₂AgBiBr₆ crystals, arising from the prolonged carrier lifetime, greatly reduced dark currents, and polaron formation.[97] The incorporation of 1% Li⁺ into Cs₂AgBiBr₆ films has demonstrated increased crystallinity, improved morphology, and a reduction of defects, originating from the higher electronic chemical potentials and higher interface wettability of Li⁺ doped Cs₂AgBiBr₆.[98] Organic-inorganic hybrid double perovskite with A-site cations comprised of linear CH₃NH₃ molecules can also be synthesized and such a material, (MA)₂AgBiBr₆ expresses a slightly decreased bandgap with a distorted lattice. This is because the bonding interaction between MA molecules and inorganic frameworks will alter the bond lengths of Ag–Br and Bi–Br and hence result in a dispersed energy level of bonding state.[99]

B-site and X-site engineering seem more effective for changing the bandgap because the Ag, Bi, and halide orbitals contribute significantly to the energy bands of Cs₂AgBiBr₆. A straightforward way to achieve this is to use trivalent or monovalent metals which have similar ionic radius with Bi³⁺ and Ag⁺ to substitute B sites. Indeed, through alloying with In³⁺ or Sb³⁺, the indirect bandgaps of bulk Cs₂AgBiBr₆ (2.12 eV) have been altered to 2.27 and 1.86 eV, respectively, which is caused by the different atomic configurations of In and Sb. Note that for bulk double perovskite, a high alloying proportion of In³⁺ (>0.75) or Sb³⁺ (>0.35) results in an unstable perovskite because of its high formation energy and small ionic radius, but this challenge can be overcome by synthesizing colloidal nanocrystals.[92] However, most of the In and Sb alloyed samples show reduced PL intensity, suggesting the presence of relatively deep
defect states. Sb/Bi alloyed thin films have been fabricated by decreasing the annealing temperature and time, which processes a reduction in the bandgap of 170 meV (from 2.25 to 2.08 eV).[100,101] Karunada and co-workers also proved that dilute alloying of thallium (Tl, 0.75%) can greatly reduce the bandgap by 0.5 eV; however, Tl is much more toxic than Pb.[59] So, they further utilized less toxic Sn[2+] (compared with Tl) to synthesize Sn-doped Cs2AgBiBr6 and achieved a very promising bandgap of 1.48 eV. But Sn oxidation will make the Sn-doped Cs2AgBiBr6 films sensitive to the ambient atmosphere and make it difficult to precisely control the doping percentage.[102]

X-site halide alloying is also capable of altering the bandgap. Chloride can be mixed with bromide at any ratio, with corresponding bandgaps of Cs2AgBiBr6-xClx varying from 2.19 eV (x = 0) to 2.77 eV (x = 6). This bandgap increase is because chloride is more electronegative and thus Cl 3p energy level lowers the valence band position.[103] Interestingly, the mixing of chloride and bromide does not change the PL emission peak significantly, possibly because of the large electron-phonon coupling and broad STE emission which is not substantially dependent on halide composition.[104,105] Unfortunately iodide can only be incorporated into bromide or chloride lattice at low concentration (<3 mol%) because higher alloying level results in non-perovskite phases.[104] Additionally, mixing sulphide and bromide (Cs2AgBiBr6-xSx) is demonstrated to slightly contract the bandgap by shifting up the valence band edge.[106]

Recently, we have reported an effective way to enhance the light harvesting of Cs2AgBiBr6 by using Cu doping.[107] Figure 6a presents the absorption of Cs2AgBiBr6 crystals with different Cu molar concentrations to Ag in precursors. Cu doping changes the crystal color from red to black, and the corresponding absorption is enhanced with a new tail absorption edge extended to 860 nm. Furthermore, the PL spectra of doped crystals are similar to pristine samples (Figure 6b) and no peak shift is observed. Combined with the decreased PL intensity, shorter PL lifetime, and DFT calculation for Cu-doped samples, we claim that Cu doping barely changes the bandgap but instead, increases the absorption by introducing defect/sub-bandgap states. To understand how Cu exists in the crystal, 133Cs and 209Bi solid-state nuclear magnetic resonance (ssNMR) is conducted with results shown in Figure 6c,d. A small shoulder peak appears at δs= 83.4±0.5 ppm for 133Cs NMR spectrum, implying that there exist two crystallographic positions of Cs+ ions and the extra position is related to the presence of Cu+/Cu2+ ions. Further analysis of the 209Bi NMR spectrum reveals a broad signal at δs= 5500 ppm with a spin-spin interaction JBiBi = 1341 Hz, which suggests a different environment of Bi3+ ions caused by the replacement of Ag+ ions by Cu+/Cu2+ ions. Therefore, the underlying mechanism is revealed. A small amount of Cu, i.e., 1%, can be inductively coupled plasma mass spectrometry (ICP-MS), is doped into the crystal lattice, and substitutes the Ag position in the form of Cu+/Cu2+ ions and introduces sub-bandgap states which contribute to the much-improved absorption. Although the Cu-doping barely affects the bandgap, the further photoconductive measurement confirms the near-IR light-responsive property of the Cu-induced sub-bandgap states, suggesting the potential for application in photo detection. Additionally, magnetic ions such as Fe3+ can also be alloyed with Bi3+ or In3+ to decrease the bandgap of double perovskites, however, the Fe3+ alloyed samples are less likely to be used in optoelectronic fields because of the PL quenching effect of Fe3+.[108–110] Instead, they offer possibilities for potential spin-electronic applications, which will be discussed later.

Dimensional reduction and tuning the order parameter are useful bandgap engineering tools as well. As mentioned before, dimensional reduction offers plenty of opportunities to create novel double perovskites with chemical and structural diversity. The reported optical bandgaps of layered Cs2AgBiBr6 derivatives are larger than their 3D counterpart. Typical layered double perovskites such as (PA)xAgBiX6 (RP phase, n = 1), (PA)2CsAgBiX7 (RP phase, n = 2) and (BDA)2AgBiX6 (DJ phase, n = 1) process bandgaps of 2.41, 2.32, and 2.43 eV, respectively.[10] The organic cation orbitals do not contribute to the band edges, but they can interact with the halides in the inorganic layer which then, in turn, influence the bandgaps.

Apart from the aforementioned methods, it is possible to intentionally tune the order-disorder parameter through growth modulation or external pressure treatment to alter the bandgap. We have reported a relatively small bandgap of 1.72 eV for bulk Cs2AgBiBr6 crystals under ambient conditions. The bandgap-narrowed crystal is achieved by carefully controlling the growth condition, i.e., the evaporation rate of hydrobromide solution. As marked in Figure 6e, the DP-150 (double perovskite with an evaporation temperature of 150 °C) sample presents an obvious red shift of absorption edge from 625 to 715 nm. The bandgap narrowing is verified by the PL spectra (Figure 6f), showing a consistent red shift of PL peak with a faster PL decay (spectra not shown here). Considering that the temperature is the only difference when preparing the crystals, Ag-Bi disorder is assigned as the origin of defect states and bandgap narrowing. Further calculation proves the assumption, revealing the disordered-lattice-induced Ag-Br-p and Bi-p/Br-p defect states emerge from valence band edge to bandgap, and from conduction band edge to bandgap, respectively.[18]

The typical optical indirect/direct bandgaps of various Cs2AgBiBr6 and its doped/alloyed and low dimensional derivatives are summarized in Figure 6g. Direct bandgaps can be achieved from some low-dimension structures such as the (BA)2AgBiBr6 and (AE2T)2AgBiI6. In fact, it is expected that future reliable direct bandgaps, which do not suffer from increased defects, poor stability, or increased toxicity, shall be achieved through clever doping/alloying methods to change the perovskite band structure. However, presently the available bandgaps for Cs2AgBiBr6 in ambient conditions can already be tuned from 1.4 to 2.85 eV offering the potential for a wide range of optoelectronic applications.

4. Wide Application of Cs2AgBiBr6

4.1. Solar Cells

In 2016, Slavney et al. reported the first synthesis of non-toxic and stable Cs2AgBiBr6 which presents a long carrier lifetime of 660 ns and an indirect bandgap of 1.95 eV, suggesting promise for photovoltaic applications.[39] From then, Cs2AgBiBr6 solar cells (Shockley-Queisser efficiency limit: ≈16%) have attracted
much research interest. Theoretically, the spectroscopic limited maximum efficiency (SLME) of Cs$_2$AgBiBr$_6$ solar cells is 7.92%, impacted by its relatively large and indirect bandgap. A higher simulated power conversion efficiency of 11.17% can be achieved by gently engineering the valence band offset between the Cs$_2$AgBiBr$_6$ absorber (600 nm) and Cu$_2$O HTL. Still yet more encouragingly, through proper selection of electron transport layer and HTL to avoid built-in voltage loss, optimized devices with a structure of FTO/ZnO/Cs$_2$AgBiSb$_{0.25}$Br$_6$(400 nm)/Cu$_2$O/Au can generate a simulated 18.18% efficiency, thus highlighting the great potential of Cs$_2$AgBiBr$_6$ based lead-free solar cells.

Experimentally, the first Cs$_2$AgBiBr$_6$ solar cell (mesoporous structure, PCE = 2.43%) was reported in 2017 using a spin-coated Cs$_2$AgBiBr$_6$ film as the absorber, demonstrating the suitability of double perovskites for photovoltaic devices.

Figure 6. a) Normalized UV-vis absorption and b) photoluminescence of pristine Cs$_2$AgBiBr$_6$ (Cu-0) and Cs$_2$(Ag:Cu)BiBr$_6$ (Cu-1, Cu-10, Cu-30, and Cu-50) double perovskites. Inset is the optical images of representative crystals. c) The $^{133}$Cs SD/MAS NMR and $^{133}$Cs Hahn-echo MAS NMR spectra of Cs$_2$(Ag:Cu)BiBr$_6$(Cu-50). d) The $^{209}$Bi ssNMR of Cs$_2$(Ag:Cu)BiBr$_6$(Cu-50), which were conducted at static conditions. a–d) Reproduced with permission. Copyright 2020, The Authors. Published by Wiley-VCH GmbH. e) Normalized UV-Vis absorption spectra of DP-60 and DP-150 Cs$_2$AgBiBr$_6$ single crystals with inset showing the optical images of crystals. f) Normalized PL spectra of DP-60 and DP-150 Cs$_2$AgBiBr$_6$ single crystals at RT. e) and f) Reproduced with permission. Copyright 2020, The Authors. Published by Wiley-VCH GmbH & Co. KGaA, Weinheim. g) Optical bandgaps of various Cs$_2$AgBiBr$_6$ and its derivatives. The samples without special statements are crystals. The blue spheres and circles represent indirect and direct bandgap, respectively. CPA is chloropropylammonium and AE2T is 5,5-diylbis(aminoethyl)-[2,2-bithiophene].
As discussed previously, the carrier diffusion length of Cs$_2$AgBiBr$_6$ crystals is more than 700 nm, and how about the diffusion length in a thin film? To answer this question, our group has carried out TRPL experiments to quantify the magnitude. We prepared PC$_{61}$BM ETL and Spiro-OMeTAD HTL on top of Cs$_2$AgBiBr$_6$ films and then analyzed the corresponding decay dynamics to obtain PL lifetime quenching ratios (Figure 7a). By using a charge-carrier extraction model based on diffusion,\cite{116} we estimated a 110 ± 20 nm photoexcitation diffusion length for electrons and holes.\cite{94} It is worth noting that the hole’s diffusion length here is a little smaller than the electron’s. This long diffusion length suggests promising performance for Cs$_2$AgBiBr$_6$ solar cells with a planar structure. Following this, we demonstrated the first planar Cs$_2$AgBiBr$_6$ solar cells with an architecture of ITO/TiO$_2$/Cs$_2$AgBiBr$_6$(205 nm)/Spiro-OMeTAD/Au. The optimal device yields a 1.22% PCE with an open-circuit voltage ($V_{OC}$) of 1.06 V and a high fill factor (FF) of 74% (Figure 7b). Notably, there is almost no hysteresis in the planar device, suggesting less trapping/detrappping or ion migration. However, the maximum short-circuit current density ($J_{SC}$) is only 1.7 mA cm$^{-2}$, which is lagging far behind the simulated values. It is expected that the $J_{SC}$ might be increased by improving the absorber quality and enhancing the extraction efficiency of ETL and HTL. For instance, the low-pressure assisted deposition process, anti-solvent dropping technology, thermal evaporation method, or composition stoichiometry engineering can improve the film quality (dense and smooth morphology with large grain size and high crystallinity), generating moderate PCEs.\cite{45,84,85,33,118} Furthermore, the above-mentioned promising bandgap narrowing methods such as using Sb alloying or disorder arrangement have limited reports for solar cell applications, possibly because difficulties are encountered when forming high-quality thin films or decreasing the bandgaps.

In fact, there have been a recent number of device engineering methods that have succeeded in boosting the performance of Cs$_2$AgBiBr$_6$ solar cells. Firstly, to increase the light absorption of Cs$_2$AgBiBr$_6$ solar cells, researchers have turned to apply a dye interlayer (N719) or photoactive ETL/HTL (carboxy-chlorophyll derivative (C-Chl), zinc chlorophyll derivative) into the device.\cite{11,47,119} As shown in Figure 7c, the incorporation of C-Chl on top of the mesoporous TiO$_2$ increases the EQE significantly over nearly the whole spectrum, especially between 650–750 nm, correlating well with the absorption of the C-Chl film. Combining with its other advantages such as reducing defects, accelerating charge extraction, and suppressing recombination, C-Chl results in a clear improvement of the photocurrent density. This lead to an outstanding efficiency of 3.11% with a $V_{OC}$ of 1.04 V, a $J_{SC}$ of 4.09 mA cm$^{-2}$, and an FF of 73%, which is by far the highest PCE reported for Cs$_2$AgBiBr$_6$ solar cells (Figure 7d).\cite{11} It should be noted this improvement of $J_{SC}$ and PCE is partially due to the contribution of additional sunlight absorption of the photosensitizer rather than intrinsic improvements to the Cs$_2$AgBiBr$_6$ absorber layer.
Next, to enhance the carrier extraction efficiency in Cs₂AgBiBr₆ solar cells, one can properly select ETLs/HTLs with fast and balanced charge transport properties.[80] Solution-processed compact TiO₂ layer usually has a relatively low electron conductivity and mobility, which results in charge accumulation at the interface or in ETL. As such, Li et al. have doped single-layered MXene nanosheets into TiO₂ to fabricate Ti₃C₂Tx@TiO₂ multilayered ETL for planar Cs₂AgBiBr₆ solar cell.[120] MXene nanosheets not only improve the conductivity, electron extraction and decrease the nonradiative recombination sites in TiO₂ but also modifies the surface wettability of ETL and promotes crystallization of Cs₂AgBiBr₆ films. Notably, Cs₂AgBiBr₆ solar cells are very stable in the ambient atmosphere under continuous AM 1.5G sunlight irradiance, and the PCE retains 93% of its initial value (2.8%) after 15 days for devices based on Ti₃C₂Tx@TiO₂ ETL (Figure 7e). Indeed, even at high temperatures (85 °C, 0% RH), Cs₂AgBiBr₆ solar cells can remain 80% of their initial efficiencies after 60 days.[98]

Despite these developments in Cs₂AgBiBr₆ solar cells, it is clear that the current PCE (below 3.13%) is still far from satisfying (Figure 7f), either for single-junction or tandem solar cells. Therefore, if significant improvements are to be made there must also be a focus on the intrinsic properties of the Cs₂AgBiBr₆ layer. Firstly, when looking for further improvements to PCE it is worth studying the V_OC. In semiconductor solar cells, the achievable V_OC is defined by the difference between the split quasi-Fermi levels of electrons and holes.[121] The typical V_OC deficit ratio (V_OC/E_0) of Cs₂AgBiBr₆ solar cells is 0.56 (1.17 V/2.12 V), which is comparable to organic solar cells (0.55) but lower than lead-based solar cells (0.69) and traditional amorphous silicon or GaAs thin-film solar cells (0.80).[122]

To further boost the V_OC and reduce the photon energy loss of Cs₂AgBiBr₆ solar cells, the limiting mechanisms must be understood. The V_OC loss (difference between V_OC and the radiative limit, i.e., V_OC_rad) relationship in Cs₂AgBiBr₆ solar cells can be described as:[121-125]

\[
\Delta V_{OC} = V_{OC,rad} - V_{OC} = -\frac{kT}{q} \ln \left( \frac{E_{QE_{EL}}}{J_{SC}} \right)
\]

\[
V_{OC,rad} = \frac{kT}{q} \ln \left( \frac{J_{SC}}{J_{0,rad}} + 1 \right)
\]

\[
E_{QE_{EL}} = \frac{J_{0,rad}}{J_{0,rad} + J_{SC,rad}}
\]

where kT/q is the thermal voltage. E_{QE_{EL}} is expressed as the ratio of radiative currents to total recombination currents and can be quantified by measuring the EQE of electroluminescence of solar cells under injection current densities equal to J_{SC}. J_{0,rad} is the saturation current density for radiative recombination and J_{SC,rad} is the non-radiative recombination currents. Therefore, the voltage losses due to non-radiative recombination in Cs₂AgBiBr₆ solar cells can be quantified by either calculating the radiative limit voltage or measuring the E_{QE_{EL}} of the complete cells. The V_OC_rad represents the thermodynamic voltage limit for Cs₂AgBiBr₆ solar cells, and can be determined from the EQE by combining electroluminescence and Fourier transform photocurrent spectroscopy. The E_{QE_{EL}} can be affected by many factors such as the charge injection balance, interface layer recombination, and light out-coupling efficiency. The V_OC_rad and E_{QE_{EL}} of Cs₂AgBiBr₆ solar cells have been reported very recently, revealing a V_OC_rad of 1.6 V and an EL yield of 10^{-8}.[126] While the V_OC_rad and E_{QE_{EL}} for In-doped Cs₂AgBiBr₆ solar cells is recently determined to be 1.36 eV and 10^{-10} respectively, for an absorber with a bandgap of 2.23 eV.[127]

The low V_OC_rad and EL yields call for further studies to unravel the origin and provide guidance of increasing the radiative efficiency. Alternatively, one can use the intrinsic property of the material, i.e., the photoluminescence quantum yield (PLQY), to understand the non-radiative recombination of the absorber. PLQY can be written as PLQY = (J_{SC} + J_{rad} - J_{EL} + J_{0,rad}) / J_{SC}, where n is the carrier density, k₁ is the first-order trap-mediated recombination rate constant, k₂ is the second-order radiative recombination rate constant, and k₃ is the third-order Auger recombination rate constant. The PLQY of Cs₂AgBiBr₆ films presents a very low value at RT, i.e., 0.01% at high excitation power density of 500 mW cm⁻²,[48] demonstrating that the main recombination pathways in Cs₂AgBiBr₆ are non-radiative (trap-mediated recombination and Auger recombination). Auger recombination dominates at higher carrier densities (e.g., >10¹⁷ cm⁻³) and can be reduced by compositional modulation and hence it has relatively little effect on photovoltaic applications,[128] while trap-related non-radiative recombination is related to the perovskite film quality and the interface between the absorber and ETL/HTL. In principle, improving the PLQY or E_{QE_{EL}} of Cs₂AgBiBr₆ films or devices would reduce/increase the non-radiative/radiative recombination and allow for a lower voltage loss. Therefore, detailed approaches including controlling the perovskite stoichiometry, increasing perovskite crystallinity, increasing the grain sizes, and using more efficient ETLs/HTLs or interface interlayers show promise to minimize the voltage loss. Additionally, developing effective passivation methods to heal the defects/traps is important for further V_OC improvement in Cs₂AgBiBr₆ solar cells.

However, looking beyond the V_OC, the small current density, which is less than 6 mA cm⁻², is the main performance-limiting factor for Cs₂AgBiBr₆ solar cells. The reason is attributed to the lower absorption coefficient from the indirect wide bandgap and insufficient charge collection. As discussed previously, the absorption of Cs₂AgBiBr₆ film is very weak in the third wave-length range (with an edge at ≈610 nm), as assigned to the indirect bandgap absorption. Most of the light absorption is contributed by the short wavelength range, i.e., the direct bandgap absorption and the Bi orbital transition. As such, enhancement of light absorption is required to boost the limited current density and efficiency. Therefore, bandgap engineering is an important area for research, as it has the potential to solve these problems. Besides, we can use a thicker active layer to absorb more incident light. In that case, we need to make sure that Cs₂AgBiBr₆ films have a long diffusion length in thicker films (i.e., the minority diffusion length is higher than half of the thickness of film) to achieve high current output. The next step is to enhance the charge collection efficiency and guarantee a balanced electron/hole charge transport. Longo and co-workers have fabricated planar n-i-p Cs₂AgBiBr₆ solar cells and analyzed the EQE spectrum via illumination through the n-side and...
p-sides of the cells. The measured p-side EQE is much lower than the n-side EQE, which means that when electrons must travel a long distance across the active layer they cannot be collected efficiently. This reveals that Cs₂AgBiBr₆ suffers from much lower electron-diffusion length (about 30 nm) than hole-diffusion length (>150 nm).[129] A strategy to overcome the short electron diffusion length is to eliminate the energetic disorder and the electron traps. It is noted that there exists a discrepancy in charge transport properties, which may be caused by the different synthesis protocols.[94,129]

Although Cs₂AgBiBr₆ solar cells have experienced advancements in their PCE, it is apparent that more research work is needed to match those of other technologies. Indeed, alterations to device architecture yield greatly improved performances, but it must be noted that further improvement to Cs₂AgBiBr₆ absorber layers by reducing non-radiative recombination, decreasing the optical bandgaps, and increasing the charge collection efficiency present themselves as the most promising approaches to seeing further improvements in the performance of Cs₂AgBiBr₆ solar cells.

### 4.2. Photodetectors

Photodetectors that capture light signals and convert them into electrical signals are the cornerstone component of numerous applications including optical communications, biomedical imaging, non-destructive inspection, and machine vision.[130,131] Conventional photodiode and phototransistor detectors are based on silicon and III–V semiconductors, which suffer from broad spectral photosresponse and relatively high manufacturing costs. Solution-processed perovskites offer its notable advantages of processing versatility and exceptional optoelectronic properties including high absorption with tuneable bandgaps, high charge carrier mobilities, and low binding energies, making them suitable for light detecting applications.[132–135]

Among all the perovskites, Cs₂AgBiBr₆ stands out as a promising candidate because of its excellent stability and high resistivity, which is important to obtain a stable and nontoxic photodetector with a low dark current.[136–138] In general, to evaluate the performance of photodetectors, parameters including response time, responsivity, detectivity, linear dynamic range and stability are important. The response time can be calculated by a standard square wave method, i.e., the rise/fall time is defined as the time for the photocurrent to increase/decrease from 10%/90% to 90%/10% of the light response peak or by a transient photocurrent method, i.e., it is defined as the time for the photocurrent decrease from the peak to about 1/e after a single exponential fit for the decay curve. And the responsivity (R) at a certain wavelength λ can be expressed as:

\[
R = \frac{J_{\text{ph}}}{P} = \frac{EQE \times \lambda}{h \nu}
\]

(11)

where \(J_{\text{ph}}\) is the photocurrent density, \(P\) is the incident light intensity, \(EQE\) is the external quantum efficiency of the photodetector, \(h\) is the Planck constant and \(\nu\) is the speed of light. The specific detectivity (\(D^*\)), as the most important figure of merit of a photodetector, is defined by:

\[
D^* = \frac{\sqrt{AB}}{i_R/R}
\]

(12)

where \(A\) is the active area, \(B\) is the bandwidth of the noise and \(i_R\) is the measured dark current noise. The linear dynamic range (LNR), indicating the linear correlation between photocurrent and light intensity in a certain spectral range, is described by:

\[
LNR = 20 \times \log \frac{J_{\text{ph}}}{J_d}
\]

(13)

where \(J_{\text{ph}}\) is the photocurrent density measured at a light intensity of 1 mW cm⁻², \(J_d\) is the dark current density. The stability of photodetectors is mainly assessed by the device long-term stability to air (oxygen, moisture) and continuous illumination.

There are mainly three types of photodetector structure, i.e., photodiode, phototransistor, and phototransistor,[139] as depicted in Figure 8a. Photodiodes, which have a narrow charge transit distance and inner electric field, usually have fast response speed, low noise, and large detectivity, but suffer from low responsivity and EQE. By contrast, phototransistors show large responsivity/EQE because of the photoconductive gain (defined as the ratio of the lifetime of trapped carriers to the transit time of the transport carriers), but shows low response time and small detectivity.[140] In comparison, phototransistors present balanced parameters among these three structures.[111] Motivated by the progress made in solar cells, Cs₂AgBiBr₆ was employed as a photoactive layer for symmetrically structured photoconductive detector.[140] The photodetector is fabricated using Si/SiO₂ as substrates, one-step solution-processed Cs₂AgBiBr₆ thin film as absorbers, and fingers of Au as contact electrode, forming a planar metal-semiconductor-metal structure (inset of Figure 8b). Under illumination with proper energy, Cs₂AgBiBr₆ film will generate electron-hole pairs, then the electron-hole pairs separate and are collected by opposite electrodes with help of the external electric field, producing an efficient photodetector. The device shows a maximum \(R\) and \(D^*\) of 7.01 A W⁻¹ (Figure 8b) and 5.66 × 10¹¹ Jones (1 Jones = 1 cm Hz⁻¹ W⁻¹) at incident irradiance (520 nm) and intensity of 0.0143 mW, indicating a promising weak light signal behavior (high on/off ratio: 2.16 × 10⁶). More importantly, the detectors possess remarkable operational stability over aging tests in ambient air with continuous bias voltage and light irradiation (Figure 8c). To decrease the current leakage and increase the response speed in photodetectors, photodiodes with p-i-n/n-i-p structure have been employed. We have demonstrated an efficient Cs₂AgBiBr₆ photodiode detector by optimizing the HTL and ETL and reducing the trap state densities in devices. The combination of a SnO₂ ETL and TFB HTL outperform other candidates and generate lower capacitances with much-decreased trap state densities (Figure 8d), mainly because of the superior transport capacity of SnO₂ ETL and additional passivation effect of TFB HTL. Benefiting from the optimized interface and dark current density, we have achieved photodetectors with outstanding parameters including a high \(D^*\) of 3.29 × 10¹² Jones at 445 nm (Figure 8e), a high LDR of 193 dB (from 2 × 10⁻¹¹ to 0.15 W cm⁻²), and a fast response time of 17 ns, which are comparable or higher than those of the best-performing
The light absorber quality is an important factor for determining the device’s photodetection parameters. By modifying the commercial FTO substrates with ultra-thin metal oxides including Al$_2$O$_3$, TiO$_2$, and NiO$_x$, the quality of Cs$_2$AgBiBr$_6$ films has been improved significantly with increased grain size and high uniformity. This improvement mechanism is shown by XPS analysis, revealing that the Cs$_2$AgBiBr$_6$ lattice bonds with the oxygen atoms from the metal oxides (Bi-O interaction). Specifically, the modified photodetector based on FTO/NiO$_x$/Cs$_2$AgBiBr$_6$/ETL/Au exhibits high light current (Figure 8f) and very low dark current ($1.3 \times 10^{-11}$ A), yielding a high $D^*$ of $1.2 \times 10^{13}$ Jones. More recently, the photodetection performance has been further improved using a 2D Cs$_2$AgBiBr$_6$ nanoflakes grown by a space-confined method as the active layer. The nanoflakes exhibits significantly enhanced light-matter interaction and thus enables high-performance photodetection with an $R$ of 54.6 A W$^{-1}$ and a remarkable $D^*$ of $7.4 \times 10^{14}$ Jones.

Table 1 summarizes the key parameters of Cs$_2$AgBiBr$_6$ photodetectors together with representative lead-based/lead-free photodetectors. The Cs$_2$AgBiBr$_6$ has shown a decent performance with a wide range photocurrent (265–620 nm), a maximum $R$ of 54.6 A W$^{-1}$, a maximum $D^*$ of $7.4 \times 10^{10}$ Jones, a maximum LDR of 193 dB with a detecting limit of tens of pW cm$^{-2}$ and the shortest response time of 17 ns, which is very promising for light detection and imaging. To further improve the photodetector performance for practical applications, the focus must be paid to the material (absorber and interlayer) engineering and architecture engineering. The perovskite absorber/active layer should be considered first, as the relatively poor absorption of Cs$_2$AgBiBr$_6$ would limit the further improvement of the photodetector light response. For this, strategies such as bandgap modulation and integration of plasmonic nanostructure or optical waveguide can be used. Synthesis of high-quality absorber films or single crystals with optimized morphology (smooth, pinhole-free, fewer grain boundaries), high crystallinity, high charge mobility, and long carrier lifetime is vital for improving the detecting performance. Defects in devices, which mainly come from the absorber and the ETL/HTL interface/surface, need to be carefully removed/passivated to minimize the loss of photo-charge carriers and suppress the leakage current of photodetectors. It is worth noting that Cs$_2$AgBiBr$_6$ materials, especially its low-dimension derivatives, may present tuneable wavelength-dependent photodetection (from UV to NIR), which are rarely reported and thus need future investigation. In terms of device architecture engineering, there are also several further improvements to be made. Currently, it remains challenging to obtain a high responsivity and a fast response speed simultaneously for Cs$_2$AgBiBr$_6$ photodetectors. Therefore, experiments on Cs$_2$AgBiBr$_6$ phototransistors are needed to verify if they can deliver a balanced detecting performance. Additionally, heterojunction or multi-junction structures, for example, combining perovskite with low-bandgap polymers, can be employed to realize absorption compensation or tuneable wavelength photodetection. Through rational design and manipulation of the materials and
architectures, continuous rising of Cs$_2$AgBiBr$_6$ photodetector performance is highly expected.

### 4.3. X-Ray Detectors

Apart from photodetectors, X-ray detectors also have important and broad applications in non-destructive inspection, medical diagnostics, defence, and scientific research. Typically, there are two strategies to detect X-rays, i.e., direct detection which converts the X-ray radiation to electrical currents, and indirect detection which transforms the radiation into UV/visible light followed by a light-electric signal conversion using photodiodes, with the corresponding structure shown in Figure 9a. Traditional X-ray detectors rely on inorganic semiconductors such as direct-type materials Si, amorphous Se, HgI$_2$, PbI$_2$, CdZnTe, and indirect-type scintillator Bi$_4$Ge$_3$O$_{12}$, CsI: Tl and YAlO$_3$: Ce, suffering from limitations of low stopping power, poor stability, high toxicity, and complex/costly fabrication.

In recent years, perovskite, especially lead-free perovskites, have emerged as efficient X-ray detector materials because of their intrinsic advantages including easy fabrication, high stability, environmental friendliness and superior optoelectronic properties (high atomic number, high X-ray absorption, high charge mobility and tuneable bandgap). To evaluate the X-ray absorption capacity of certain materials, the absorption can be expressed as:

$$I_d = I_0 e^{-\alpha d}$$  \hspace{1cm} (14)$$

$$\alpha = \frac{\rho Z^4}{AE^2}$$  \hspace{1cm} (15)$$

where $I_d$ and $I_0$ represent the X-ray intensities at a thickness of $d$ and zero, $e$ is the electron charge, $\alpha$ is the absorption coefficient, $\rho$ is the density, $Z$ is the atomic number, $A$ is the atomic mass and $E$ is the X-ray photon energy. Therefore, Cs$_2$AgBiBr$_6$ perovskites with heavy metal (Bi$^{3+}$, $Z = 83$) with an average $Z$ value of 53.1 can efficiently interact with X-rays and possess a large stopping power ability.

To efficiently collect the charges, especially in direct X-ray detection, materials should have a high carrier drift length per unit electric field, i.e., the $\mu$τ product, where $\mu$ is the carrier mobility and $\tau$ is the carrier lifetime. The $\mu$τ product can be calculated from the bias-dependent photoconductivity fitting using modified Hecht equation:

$$I = \frac{I_0 \mu \tau V}{E^2} \left[ 1 - \exp \left( -\frac{L^2}{\mu \tau V} \right) \right] \frac{1}{1 + \frac{L}{\mu \tau}}$$  \hspace{1cm} (16)$$

where $I$ is the photocurrent, $I_0$ is the saturated photocurrent, $L$ is the thickness, $V$ is the applied bias and $s$ is the recombination velocity. Typical X-ray detection parameters include the sensitivity and detection limit. Sensitivity represents the response ability of detectors at a given amount of radiation and is expressed by the formula:

$$R_s = \frac{I_p - I_s}{D \times S}$$  \hspace{1cm} (17)$$

where $R_s$ is the sensitivity, $I_p$ is the induced photocurrent, $I_s$ is the dark current, $D$ is the irradiation dose rate of X-ray and $S$ is the effective area of the device. And the standard detection limitation is defined by the International Union of Pure Applied Chemistry as the dose rate producing a signal which is three times of the noise.

Tang and co-workers first reported a Cs$_2$AgBiBr$_6$ single-crystal direct X-ray detector with a low detection limit in 2017. As shown in Figure 9b, Cs$_2$AgBiBr$_6$ crystals exhibit a high attenuation efficiency for 50 KeV hard X-ray photons and hence a small thickness of 1.18 mm is enough for Cs$_2$AgBiBr$_6$ crystal to attenuate 99% of incident X-ray, which is superior to MAPbBr$_3$. Through thermal annealing at a moderate temperature (373 K), the order degree of the crystals has been improved and Ag/Bi antisites defects are reduced, generating high mobility and low
trap density of 11.81 cm$^{-2}$ V$^{-1}$ s$^{-1}$ and $1.74 \times 10^9$ cm$^{-3}$, respectively. Therefore, a promising $\mu \tau$ product of $6.3 \times 10^{-3}$ cm$^2$ V$^{-1}$ has been achieved, which is comparable to that of lead-based perovskites and CdZnTe. Additional surface treatment using isopropanol or ethyl acetate can further remove the surface states, decrease the surface recombination velocity, and most importantly increase the resistivity to $1.6 \times 10^{11}$ Ω cm, which is much higher than lead-based perovskite ($10^7$–$10^8$ Ω cm). The high X-ray absorption, adequate $\mu \tau$ product and high resistivity properties of Cs$_2$AgBiBr$_6$ crystals have thus finally guaranteed an impressive X-ray detection performance with very low dark current density (0.15 nA cm$^{-2}$ at 5 V) and low detection limit of 59.7 nGy air$^{-1}$ (Figure 9c).

Ion migration in perovskites can cause noise, render the baseline drift, reduce the sensitivity and limit the X-ray detection especially the imaging performance.[157] Generally, the smaller and less charged ions, which have a shorter jumping distance, or those that stay in a crystal lattice with more vacancies will migrate faster.[158,159] For Cs$_2$AgBiBr$_6$, the Br$^-$ vacancies, which have lower activation energy ($E_a$, also known as the ion diffusion barriers), are found to be the main species accounting for the migration.[10] To effectively suppress the ionic migration, BiOBr is epitaxially grown onto Cs$_2$AgBiBr$_6$ wafers (epitaxial growth model is shown in the inset of Figure 9d). BiOBr can supply additional Br$^-$ to suppress the Br$^-$ vacancies thus reducing the migration channels. The reduced migration can be reflected by the calculation of the activation energy in Figure 9d. The ion motion is in proportion to the ion conductivity and sensitive to the applied electric field. When the bias on X-ray detection devices is off, the ions accumulate at the interface between the electrode and the absorber and result in an opposite electrical field, which will therefore reduce photocurrent and cause the photocurrent decay following a function of $\mu \tau$ product and increased resistivity by BiOBr passivation enable the fabrication of high-efficiency X-ray detectors with low signal drifting, low noise, high sensitivity (250 μC Gyair$^{-1}$ cm$^{-2}$ at 0.5 V μm$^{-1}$, shown in Figure 9f), and high spatial resolution.[161]

\[
\ln(kT) = C - \frac{E_a}{k_BT}
\]

(18)

where $k$ is the decay rate of the photocurrent, $C$ is a constant, $k_B$ is the Boltzmann’s constant and $T$ is the temperature. The $E_a$ of BiOBr passivated Cs$_2$AgBiBr$_6$ wafer is then calculated to be 360 meV, much higher than the control wafers (203 meV) and slightly higher than pure Cs$_2$AgBiBr$_6$ crystals (348 meV), as shown in Figure 9d. By measuring the bias-dependent photocurrent as mentioned above, the $\mu \tau$ product of BiOBr passivated Cs$_2$AgBiBr$_6$ wafer is improved from $1.57 \times 10^{-3}$ to $5.51 \times 10^{-3}$ cm$^2$ V$^{-1}$ (Figure 9e). The combination of suppressed ion migration, increased $\mu \tau$ product and increased resistivity by BiOBr passivation enable the fabrication of high-efficiency X-ray detectors with low signal drifting, low noise, high sensitivity (250 μC Gyair$^{-1}$ cm$^{-2}$ at 0.5 V μm$^{-1}$, shown in Figure 9f), and high spatial resolution.[161]
As an emerging technology, an increasing number of lead-free Bi-based semiconductors including Cs$_2$AgBiBr$_6$ and its low dimensional derivatives and A$_2$Bi$_3$I$_7$ (A = Cs$^+$, MA$^+$ or NH$_4^+$) have been applied in direct X-ray detection and achieved very promising performances, as shown in Table 2.[146,157,162] For a perfect X-ray detector, it should possess high sensitivity, high stability, low noise current, low detection limit, and quick response time. All inorganic Bi-based materials such as Cs$_2$AgBiBr$_6$ have achieved low detection limits with decent air quick response. All inorganic Bi-based materials such as Cs$_2$AgBiBr$_6$ offer a potentially superior material system.

### 4.4. Ferroelectricity

Ferroelectric materials, featuring a switchable spontaneous electric polarization, present an exciting field of research as they are suited to many technological applications such as capacitors, data storage, and sensors.[172] Despite the established success of oxide perovskite ferroelectrics, emerging halide perovskites have the potential to produce new low-cost multifunctional ferroelectric devices, through a combination of low-temperature solution synthesis and diverse optoelectronic properties. However, it is difficult to achieve ferroelectricity in the typical 3D perovskite structure, due to the high symmetry imposed by the Goldschmidt Tolerance factor.[173] Therefore, recent works have opted for 2D perovskites that enable the symmetry breaking necessary for ferroelectric polarization to be expressed. While this has been used in lead-based perovskites to achieve favorable ferroelectric properties, stability and toxicity concerns and diverse structures mean that lead-free Cs$_2$AgBiBr$_6$ offers a potentially superior material system.

Indeed, Zhang et al. presented the first 2D ferroelectric halide double perovskite (PA)$_2$CsAgBiBr$_6$ in 2020, which undergoes a phase transition from the $P2_1/m$ paraelectric phase to a $P2_1$ non-centrosymmetric ferroelectric phase below the Curie temperature of 222 K.[174] This results in a spontaneous polarization of 1.5 $\mu$C cm$^{-2}$ due to disorder in the crystal lattice, causing the displacement of the Cs$^+$ and organic cations. While this spontaneous polarization is somewhat smaller compared to lead-based perovskite counterparts (2.9–13 $\mu$C cm$^{-2}$), developing new structure-function relationships are also important in advancing X-ray detection research.

### Table 2. Parameters of X-ray detectors based on Cs$_2$AgBiBr$_6$, its derivatives, other lead-free materials and conventional counterparts.

| Material | X-ray energy [eV] | $\mu$C product [cm$^2$ V$^{-1}$] | Sensitivity [µC Gy$^{-1}$ cm$^{-2}$] | Detection limit [nGy$^{-1}$ s$^{-1}$] | Ref. |
|----------|------------------|---------------------------------|-----------------------------------|-----------------------------------|-----|
| Cs$_2$AgBiBr$_6$ SC$^a$ | ≤ 50 K, $E_{\text{peak}} = 30$ K | 6.3 $\times$ 10$^{-3}$ | 105 (25 V mm$^{-1}$) | 59.7 (2.5 V mm$^{-1}$) | [10] |
| Cs$_2$AgBiBr$_6$ wafer | ≤ 50 K, $E_{\text{peak}} = 30$ K | 5.51 $\times$ 10$^{-3}$ | 250 (1000 V mm$^{-1}$) | 95.3 (5–10 V mm$^{-1}$) | [161] |
| LT$_{\text{H}}$Cs$_2$AgBiBr$_6$ SC | ≤ 50 K, $E_{\text{peak}} = 30$ K | – | 988 (50 V mm$^{-1}$) | – | [78] |
| Cs$_2$AgBiBr$_6$ SC | 18–100 K, $E_{\text{eff}} = 39$ K | – | 316 (6 V mm$^{-1}$) | – | [164] |
| Cs$_2$AgBiBr$_6$ SC | 50 K | 9.14 $\times$ 10$^{-4}$ | 165.6 (22.7 V mm$^{-1}$) | – | [25] |
| PEA-Cs$_2$AgBiBr$_6$ SC | 50 K | 1.94 $\times$ 10$^{-3}$ | 288.8 (22.7 V mm$^{-1}$) | – | [25] |
| (BA)$_2$CsAgBiBr$_7$ SC | 70 K | 1.21 $\times$ 10$^{-3}$ | 4.2 (5 V mm$^{-1}$) | – | [165] |
| CC$^a$-Cs$_2$AgBiBr$_6$ SC | ≤ 50 K, $E_{\text{peak}} = 30$ K | 5.95 $\times$ 10$^{-3}$ | 1974 (50 V mm$^{-1}$) | 45.7 (2.5 V mm$^{-1}$) | [166] |
| (CPA)$_2$AgBiBr$_6$ SC | 70 K | 1.0 $\times$ 10$^{-3}$ | 0.8 (5 V mm$^{-1}$) | – | [32] |
| Cs$_2$AgBiBr$_6$ film | 45 K | – | 40 (4000 V mm$^{-1}$) | – | [167] |
| Cs$_2$BiI$_4$ SC | 40 K | 7.94 $\times$ 10$^{-4}$ | 1652.3 (50 V mm$^{-1}$) | 130 (50 V mm$^{-1}$) | [168] |
| (NH$_4$I)$_2$Bi$_3$I$_7$ SC | ≤ 50 K, $E_{\text{peak}} = 22$ K | 1.1 $\times$ 10$^{-2}$ | 8.2 $\times$ 10$^{-2}$ (2.2 V mm$^{-1}$) | 55 (6.5 V mm$^{-1}$) | [157] |
| MA$_2$Bi$_3$I$_7$ SC | 100 K | 1.2 $\times$ 10$^{-3}$ | 10 620 (48 V mm$^{-1}$) | 0.62 (48 V mm$^{-1}$) | [169] |
| MA$_2$Bi$_3$I$_7$ SC | 100 K | 2.87 $\times$ 10$^{-3}$ | 1947 (60 V mm$^{-1}$) | 83 (50 V mm$^{-1}$) | [158] |
| CsPbI$_3$ SC | 80 K | 3.63 $\times$ 10$^{-2}$ | 2990 (31.25 V mm$^{-1}$) | 219 (31.25 V mm$^{-1}$) | [170] |
| MAPbI$_3$ SC | ≤ 50 K, $E_{\text{peak}} = 22$ K | – | 7.1 $\times$ 10$^{-2}$ (100 V mm$^{-1}$) | 1.5 (100 V mm$^{-1}$) | [171] |
| α-Se film | 28 K | 10$^{-7}$ | 20 (10$^4$ V mm$^{-1}$) | 5500 | [156] |

$^a$SC: single crystal; $^b$LT: low temperature; $^c$CC: controlled cooling.
(PA)$_2$CsAgBiBr$_7$ also exhibits impressive photodetection performance, with large on/off ratios ($≈10^4$), fast response rates (141 µs), and high detectivity ($5.3 \times 10^{11}$ Jones). Therefore, their work succeeded in highlighting the multifunctional potential that ferroelectric Cs$_2$AgBiBr$_6$ perovskites may possess. Gou and co-workers further reported room temperature ferroelectric in (CPA)$_4$AgBiBr$_8$.[32] This material is synthesized by modifying the A-site organic cations in a previously reported centrosymmetric (BA)$_4$AgBiBr$_8$ double perovskite.[31] The terminal CH$_3$ group of BA$^+$ is substituted for chlorine, forming asymmetric CPA$^+$ ligands that can dynamically reorientate, breaking the planar crystal symmetry, and providing the driving force for phase transition (Figure 10a). As a result, (CPA)$_4$AgBiBr$_8$ achieves room temperature ferroelectricity, undergoing a phase transition at a Curie temperature of 305 K (Figure 10b), and boosts an improved spontaneous polarization of ≈3.2 µC cm$^{-2}$ at RT (Figure 10c).

Recently, Liu et al. observed multi-axial ferroelectricity in the (BA)$_2$CsAgBiBr$_7$ perovskite system. [175] Already determined to possess an impressive X-ray response, (BA)$_2$CsAgBiBr$_7$ also demonstrates two phase transitions occurring at 273 and 375 K, resulting in low, intermediate, and high-temperature phases. The low-temperature phase (P2$_1$) is ferroelectric with the largest spontaneous polarization reported for Cs$_2$AgBiBr$_6$ perovskite: 5.2 µC cm$^{-2}$ (at 250 K). When transitioning to the centrosymmetric intermediate temperature phase (P2$_1$/m), (BA)$_2$CsAgBiBr$_7$ exhibits ferroelastic domains, and finally at high temperature (I4/mmm) the crystal domain structure disappears, forming a paraelectric state. In addition to three unique phases, (BA)$_2$CsAgBiBr$_7$ demonstrates impressive fatigue
resistance, maintaining stable polarization after $2 \times 10^7$ on/off switching cycles, implying the great potential for digital memory applications. Despite these improvements in spontaneous polarization, Cs$_2$AgBiBr$_6$ has recently been surpassed by the closely related Cs$_2$AgBiI$_6$, as the 2D double perovskite: (DFPIP)$_4$AgBiI$_6$ (DFPIP = 4,4-difluoropiperidinium).[176] This novel material displays superior spontaneous polarization of 10.5 μC cm$^{-2}$ (9.9 μC cm$^{-2}$ at RT), and a high Curie temperature of 422 K, which is more comparable to some oxide or lead-based perovskites.[177,178] Wang et al. specifically attribute this high Curie temperature to using a ring-shaped organic ligand versus the chain-like organic cations used in the previous works (Figure 10d), noting this trend applies to most 2D perovskite ferroelectric materials.[176]

Although there is limited research in this area of 2D ferroelectric lead-free double perovskites, it is clear that the diverse properties displayed by the Cs$_2$AgBiBr$_6$ system hold promise for multifunctional ferroelectric devices. Additionally, the achievement of high Curie temperatures in the closely related Cs$_2$AgBiI$_6$ system indicates that through rational design of organic cations, it is possible to produce many high-temperature and performant Cs$_2$AgBiBr$_6$ ferroelectric materials with widespread real-world applications in the coming years.

4.5. Magnetism

Magnetic perovskite semiconductors are becoming the subject of increased interest due to their potential in the emerging field of spintronics. Consequently, recent studies into lead-based perovskites have explored their magnetic properties such as spin-orbit coupling or magnetic doping/ alloying.[179,180] Now focus has begun to shift toward the lead-free Cs$_2$AgBiBr$_6$ material system from the recent reports on the promising magnetic properties of Fe$^{3+}$ alloyed Cs$_2$AgBiBr$_6$.[14,42] Cs$_2$Ag(Bi:Fe)Br$_6$ can be formed through a simple alloying process where magnetic Fe$^{3+}$ ions are distributed homogeneously throughout a 3D Cs$_2$AgBiBr$_6$ perovskite lattice as [FeBr$_6$]$^{3-}$ octahedra, replacing Bi$^{3+}$ ions.[14] We utilized electron spin resonance (ESR) in conjunction with a superconducting quantum interference device, to determine the perovskite’s paramagnetic centers and identify ferromagnetic or antiferromagnetic resonance signals within the Cs$_2$Ag(Bi:Fe)Br$_6$ crystals.[14] By conducting measurements over a range of temperatures (5–300 K), it is observed that Cs$_2$Ag(Bi:Fe)Br$_6$ exhibits diamagnetism at RT and weak magnetic susceptibility temperature dependence above 30 K. Obvious magnetic response appears below 20 K as proved by the rapid increase of magnetic susceptibility (Figure 11a).

As presented in Figure 11b, field-dependent magnetization $M(H)$ is linear with a negative slope above 50 K, consistent with the temperature-dependent magnetic susceptibility. While $M(H)$ at 2 K has a positive component at low fields saturating to $\approx\mu_{B}$ per Fe after subtracting the diamagnetic component. In addition, there is no obvious magnetic hysteresis in the $M(H)$ loop in the low fields (inset of Figure 11b). At 40 K, the crystal’s ESR signal is comprised of the sum of two paramagnetic centers, i.e., isolated Fe$^{3+}$ with tetragonal symmetry ($S = 5/2, g = 2.032$) and a defect center of unknown origin ($S = 1/2, g = 2.032$). In comparison, at 7 K, an extra broad component emerges and become dominant in the ESR spectrum (Figure 11c). The intensities of isolated Fe$^{3+}$ and $S = 1/2$ defect center are found to gradually and monotonically increase with decreasing temperature, proving that the sharp rise in the material’s magnetic response is related to the third and broad component that becomes dominant at $T <35$ K. (Figure 11d).

We postulate this broad component may be due to a weak ferromagnetic or antiferromagnetic coupling from localized regions within the crystal lattice, due to phase separated magnetic clusters or regions of high Fe$^{3+}$ composition caused by inhomogeneous alloy fluctuations. If this is the case, higher Fe$^{3+}$ alloying concentrations may yield a magnetic semiconducting lead-free perovskite, which need further investigation. This investigation into the potential magnetic properties of Cs$_2$Ag(Bi:Fe)Br$_6$ indicate that Cs$_2$AgBiBr$_6$-based alloys would be a candidate for a whole new category of lead-free perovskite-based spintronic materials. Therefore, future work is needed to better understand the origin of these properties and to obtain them at room temperature.

In addition, we also used a combination of ESR and Raman spectra to probe the structural phase transitions and the interplay between the structural, spin, and vibrational properties of Cs$_2$Ag(Bi:Fe)Br$_6$.[42] As Cs$_2$Ag(Bi:Fe)Br$_6$ underdoes a symmetry-breaking phase transition below 120 K, from a cubic to tetragonal phase, the six-fold degenerate $S = 5/2$ state of Fe$^{3+}$ splits into three Kramer doublets $M_s = \pm 1, \pm 1/2, \pm 3/2$ at zero magnetic fields, transforming the ESR spectra from a single line to multiple lines. Similarly, the symmetry reduction effect is found for the enharmonic breathing mode of the octahedra, which splits below the phase-transition temperature. This indicates a small amount of distortion due to a phase transition has a significant impact on the high spin states of the incorporated Fe$^{3+}$ ions, thus highlighting ESR and Raman techniques in probing the interplay between structural phase transitions and spin properties in lead-free double perovskites.

4.6. Other Applications

Perovskite materials are also intensively studied for LED applications. However, presently Cs$_2$AgBiBr$_6$ has shown limited potential as an emissive material for LED applications, due to its poor PL/PLQY performance. Therefore, as previously discussed, improvements to the PL/PLQY must be addressed before efficient LEDs can be realized. Some methods to achieve this are: reducing non-radiative defects, decreasing theelectron-phonon coupling, changing the bandgap from indirect to direct, or incorporating emissive dopants.

Chen et al. reported the first example of doping Yb$^{3+}$ ions into the double perovskite Cs$_2$AgBiX$_6$ ($X = Cl^-, Br^-$) NCs which endows a near-infrared emission band in addition to their intrinsic emission. The origin of this Yb$^{3+}$ induced NIR emission at 1000 nm is due to an energy transfer from Cs$_2$AgBiX$_6$ ($X = Cl^-, Br^-$) hosts to the $\mathbf{F}_{3/2}$ state of Yb$^{3+}$ ions. Thus, doping Yb$^{3+}$ or Mn$^{3+}$ cations into Cs$_2$AgBiX$_6$ ($X = Cl^-, Br^-$) would provide a unique system with tunable dual emission.[181] Schmitz and coworkers further investigated Yb$^{3+}$ and Eu$^{3+}$ lanthanide doping upon bulk hydrothermally processed Cs$_2$AgBiBr$_6$ and achieved a PLQY of 28% ($\pm 3$). The Yb$^{3+}$ doped samples display an extremely

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**Adapted from the figure captions:**

- Figure 11c: The intensities of isolated Fe$^{3+}$ and $S = 1/2$ defect center are found to gradually and monotonically increase with decreasing temperature, proving that the sharp rise in the material's magnetic response is related to the third and broad component that becomes dominant at $T <35$ K.

- Figure 11d: We postulate this broad component may be due to a weak ferromagnetic or antiferromagnetic coupling from localized regions within the crystal lattice, due to phase separated magnetic clusters or regions of high Fe$^{3+}$ composition caused by inhomogeneous alloy fluctuations. If this is the case, higher Fe$^{3+}$ alloying concentrations may yield a magnetic semiconducting lead-free perovskite, which need further investigation. This investigation into the potential magnetic properties of Cs$_2$Ag(Bi:Fe)Br$_6$ indicate that Cs$_2$AgBiBr$_6$-based alloys would be a candidate for a whole new category of lead-free perovskite-based spintronic materials. Therefore, future work is needed to better understand the origin of these properties and to obtain them at room temperature.

- Figure 12: By conducting measurements over a range of temperatures, it is observed that Cs$_2$Ag(Bi:Fe)Br$_6$ exhibits diamagnetism at RT and weak magnetic susceptibility temperature dependence above 30 K. Obvious magnetic response appears below 20 K as proved by the rapid increase of magnetic susceptibility.
high PL intensity relative to the pristine Cs$_2$AgBiBr$_6$ PL peak (at 300:1), indicating the hydrothermal synthesis method is superior for Yb-dopant sensitization compared to the nanocrystal sensitization conducted by Chen et al. (2.5:1 peak ratio, best case). Improvement in Cs$_2$AgBiBr$_6$ light emitting applications is expected through further enhancement of PL/PLQY, as observed by its closely related double perovskite Cs$_2$AgInCl$_6$.

Cs$_2$AgBiBr$_6$ has also provided new opportunities in energy-related photocatalysis. The basic photocatalytic mechanism involves the absorption of photons to generate electrons and holes, charge separation and migration to the reaction sites, and chemical oxidation/reduction reactions mediated by the photoinduced electrons and holes. Besides the traditional standards for photocatalytic materials (high light absorption, efficient charge separation, and appropriate redox ability), Cs$_2$AgBiBr$_6$ has enhanced operational chemical stability under different catalytic conditions like strong acidic/basic solutions and highly reducing/oxidizing atmospheres. Typically, Cs$_2$AgBiBr$_6$ nanocrystals could convert CO$_2$ into solar fuels such as CO and CH$_4$, affording an impressive total electron consumption of 105 μmol g$^{-1}$ over 6 h, with no H$_2$ side product detected. Beyond CO$_2$ reduction, the successful application of Cs$_2$AgBiBr$_6$ has also been demonstrated in dye degradation and H$_2$ generation. Because of its high humidity-dependence of the electrical properties, Cs$_2$AgBiBr$_6$ thin film can also work as a humidity sensor, showing fast response time (1.78 s) and recovery time (0.45 s).

5. Challenges and Future Perspectives: Where to Move on?

With the benefit of high structure-property diversity, high stability, and nontoxicity, lead-free double perovskite Cs$_2$AgBiBr$_6$ has attracted increasing research interests in recent years focusing on its fundamental material properties and wide applications, including photovoltaic conversion, light/X-ray detection, ferroelectricity, and magnetism, etc. In this review, we have systematically discussed and evaluated these fundamental optoelectronic properties and wide applications of Cs$_2$AgBiBr$_6$. From this it is clear, there remains a great opportunity for further device development based upon the lead-free double perovskite Cs$_2$AgBiBr$_6$ material system. However, there are still challenges which must be overcome as we move forward. The challenges and perspectives/research directions are briefly summarized in Figure 12 and are discussed below:
1) The bandgap tunability of Cs$_2$AgBiBr$_6$ remains an important issue and requires more research efforts to address. The indirect, wide bandgap nature, which is caused by the mixing of Ag and Bi frontier orbitals in Cs$_2$AgBiBr$_6$, currently severely limits its photovoltaic performance.$^{[189,190]}$ Attempts using element substitution of Ag or Bi have not yet efficiently solved this problem, each experiencing trade-offs. For example, Cu$^+$ or In$^+$ are promising for an indirect to direct transition, but they will form non-perovskite [CuX$_4$] tetrahedra or are unstable due to easy oxidation of In$^+$.\cite{191,192} Iodide incorporation can decrease the bandgap to 1.77 eV, however, iodide pure phases have not been experimentally synthesized yet and only a small amount (<3 mol%) of iodide can be mixed into the halides site.$^{[44,104]}$ A complete substitution of Bi$^{3+}$ with In$^{3+}$ would exhibit a direct large bandgap of 3.3 eV which suffer from parity-forbidden transition issue.$^{[63]}$ Sn alloying results in a good bandgap reduction of 0.5 eV but sacrifices the stability due to Sn$^{2+}$ oxidation.$^{[102]}$ Therefore, researchers must continue to search for suitable doping or alloying strategies to effectively manipulate the bandgap in both bulk and thin-film Cs$_2$AgBiBr$_6$.

To find promising doping/alloying elements, the selection should meet the criteria of a positive decomposition energy, a suitable tolerance factor and octahedral factor ($\tau < 4.18$, $0.44 \leq \mu \leq 0.9$), an optimal bandgap range, a small and balanced carrier effective mass. Specifically, elements which have similar ionic radius with Ag$^+$ or Bi$^{3+}$ should be considered first. Metal elements which lone-pair $s^2$ orbital configurations are also preferred because they would form double perovskites with B-sites of $s^2 + s^2$ type to ensure superior optoelectronic properties. Note that doping/alloying may sometimes result in parity-forbidden transition issues which calls for further modification to break the inversion symmetry. As reported, Sb$^{3+}$ alloying is a promising choice because Sb$^{3+}$ can elevate the VBM position, but it is still challenging to obtain high-quality phase-pure Cs$_2$AgBi$_x$Sb$_{1-x}$Br$_6$ films considering the high tendency for decomposition into 2D Cs$_3$Sb$_2$Br$_9$ impurities.$^{[193]}$ Therefore, careful design of the precursor stoichiometry and film growth optimization is vital to achieve Sb/Bi alloyed thin films with a decreased bandgap. Au$^+/$/Au$^{3+}$ are also alternative B-site metals. Using Au$^+/$/Au$^{3+}$ to substitute Ag$^+$/Bi$^{3+}$ can form stable Cs$_2$AuBiCl$_6$ (1.4 eV indirect bandgap) and Cs$_2$AgAuI$_6$ (1.289 eV direct bandgap) perovskites with low hole/electron effective masses, which are worthy of further experimental research.$^{[194,195]}$ Similar interesting lead-free halides such as Cu$_2$AgBiI$_6$ have emerged as promising solar cell absorbers with a direct bandgap of 2.06 eV, even if it is not a perovskite.$^{[196,197]}$ Low-dimensional Cs$_2$AgBiBr$_6$ derivatives also offer the possibility to transform indirect to direct bandgap and change the optoelectronic properties. The alternating arrangement of organic-inorganic structure will form quantum-confined architecture which enables a large exciton binding energy, making the low-dimensional Cs$_2$AgBiBr$_6$ derivatives potential scintillation materials. Overall, through the alteration of this current large indirect bandgap, it would be possible to improve the currently limited maximum theoretical efficiency of Cs$_2$AgBiBr$_6$ based solar cells. We should also note that although the indirect bandgap feature of Cs$_2$AgBiBr$_6$ is not preferred, it is beneficial for low carrier recombination rates and thus long minority carrier diffusion lengths, which are important factors in determining optoelectronic applications.

2) Strong electron-phonon coupling is a big concern for Cs$_2$AgBiBr$_6$ double perovskite as it significantly affects the carrier scattering, charge carrier mobility, PL linewidth broadening, PLQY, and electron-hole recombination. With more investigations, the charge-lattice scattering mechanism of Cs$_2$AgBiBr$_6$ is becoming clearer, reflecting the optical phonons (Frohlich coupling) and acoustic phonons (deformation potential) both synergistically contribute to the interaction, charge carrier localization, and the self-trapping process. Further studies are needed to understand the modulation of the electron-phonon coupling, for example, elucidating the relationship between the Jahn-Teller distortion, the B-site octahedra disordering, the structure dimensionality, and the
electron-phonon coupling in Cs$_2$AgBiBr$_6$. Various strategies including doping/ alloying, combined with heterojunction structures, dielectric confinement, and bond length compression (by chemical/mechanical pressure) are promising to reduce the electron-phonon coupling in Cs$_2$AgBiBr$_6$. Successful reduction should yield a higher current density from solar cells and photodetectors, resulting in increased efficiency and responsivity.

3) The defects in Cs$_2$AgBiBr$_6$ should be carefully suppressed. Cs$_2$AgBiBr$_6$ is prone to defect formations, especially deep-level defects. For Cs$_2$AgBiBr$_6$, the trap-state density is currently optimized to be $1.74 \times 10^5$, $2.13 \times 10^{16}$ and $9.1 \times 10^{16}$ cm$^{-3}$ for single crystals, evaporated and solution-processed thin films, respectively, which is comparable or slightly higher than the representative MAPbI$_3$ crystals and films (crystals: $7.6 \times 10^8$ cm$^{-3}$, films: $2.2 \times 10^{16}$ cm$^{-3}$). However, considering more deep-level defects exist in Cs$_2$AgBiBr$_6$, defect manipulation is more imperative. The possible antisite defects (AgBi or BiAg) and vacancy defects (Bi or Br vacancies) should be omitted to reduce non-radiative recombination. Experimental evidence is needed to fully understand the impact that defects have upon the material optoelectronic properties and device performance. Strategies of optimization on the growth condition, introducing passivation materials, or modification on device interfaces will play important roles in reducing the deep-level bulk/interface defects. A reduction in defect recombination is an effective method to reduce voltage losses and increase current density across many devices.

4) Despite Cs$_2$AgBiBr$_6$ having presented its multifunctionality in many different applications, there is still a massive scope to improve the performance. Taking solar cells as an example, the 3D structure, high stability, environmental friendliness, long carrier lifetime, and diffusion length have made Cs$_2$AgBiBr$_6$ attractive in the photovoltaic research field. However, current devices are limited by their low JSC and VOC, enhancing light absorption, reducing trap-related non-radiative recombination, and improving charge extraction efficiency will be the key steps to achieve better performance. In addition, using novel structures such as p-n or p-i-n homojunctions can guarantee a high-quality interface and perfect grain orientation, which will improve charge extraction in Cs$_2$AgBiBr$_6$ solar cells. There is the opinion that the wide and indirect bandgap will rule out the photovoltaic applications, but we hope that through the aforementioned methods, a significant breakthrough in the efficiency, especially the current density, will be realized in the near future. In fact, Cs$_2$AgBiBr$_6$’s wide bandgap may actually allow for alternative applications such as promising semi-transparent or tandem photovoltaics. Apart from solar cells, it is apparent that Cs$_2$AgBiBr$_6$ presents an exciting opportunity for many single/multifunctional applications, such as photodetectors, X-ray detectors, ferroelectric data storage, magnetic spintronics, light emission, photocatalysis, etc. Therefore, through continued investigation on rational design and manipulation of materials and devices, the performance of these diverse applications will be taken to a new level, thus, enabling the wide-scale commercialization of next-generation, non-toxic, stable, and efficient lead-free perovskite-based devices.

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Conflict of Interest

The authors declare no conflict of interest.

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