Bandgap Engineering of Lead-Free Halide Double Perovskites

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During the course of research underlying the thesis, Fuxiang Ji was enrolled in Agora Materiae, a multidisciplinary doctoral program at Linköping University, Sweden.

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Abstract

Lead-free halide double perovskites (HDPs, $A_2B^I B^{III}X_6$) with attractive optical and electronic features are regarded as one of the most promising alternatives to overcome the toxicity and stability issues of lead halide perovskites. They provide a wide range of possible combinations and rich substitutional chemistry with interesting properties for various optoelectronic devices. However, the performance of state-of-the-art lead-free HDPs is not yet comparable to that of lead halide perovskites, especially in the photovoltaic field. One of the main reasons for this is that HDPs usually have large and/or indirect bandgaps, which limit their optical and optoelectronic properties in the visible and infrared region. In this thesis, we attempt to modify the bandgap and optical properties of HDPs using metal doping/alloying and crystallization control, as well as provide detailed understanding of the alloying at the atomic level. We also observe significant changes of the bandgap of HDPs at different temperatures (i.e., thermochromism) and uncover the reasons behind it.

We first adopt the metal doping/alloying strategy to alter the absorption properties of benchmark HDPs $Cs_2AgBiBr_6$. By introducing Cu as the dopant in $Cs_2AgBiBr_6$, we significantly broaden the absorption edge from around 610 nm to around 860 nm. Systematic characterizations indicate that Cu doping introduces defect states (sub-bandgap states) in the bandgap, without changing the bandgap of $Cs_2AgBiBr_6$. Interestingly, these sub-bandgaps can generate considerable amount of band carriers upon optical excitation, making these double perovskites promising for near-infrared light detection.

In parallel with the material modification using the metal doping/alloying strategy, the fundamental understanding of these doped/alloyed double perovskite is also of critical importance. In the second paper, we reveal the atomic-level structure of alloyed double perovskites by presenting a series of double perovskite alloys with the chemical formula $Cs_2AgIn_{1-x}Fe_xCl_6$ ($x = 0-1$) showing tunable bandgaps in the range of 2.8-1.6 eV. Our results show that Fe^{3+} substitutes In^{3+} in the lattice with the formation of $[FeCl_6]^{3-} \cdot [AgCl_6]^{5-}$ domains, which grow larger gradually as the Fe^{3+} concentration increases. It is noted that these domains could be further connected to form microscopically segregated Fe^{3+} -rich phases in the double perovskite alloys.

To narrow the bandgap of $Cs_2AgBiBr_6$, we also develop a crystallization control approach, where high temperature is employed to assist the single crystal growth. By simply increasing the crystal growth temperature from 60 °C to 150 °C, the bandgap of

$\text{Cs}_2\text{AgBiBr}_6$ crystals can be reduced from 1.98 eV to 1.72 eV, which is the lowest reported bandgap for $\text{Cs}_2\text{AgBiBr}_6$ at ambient conditions. The underlying reason is hypothesized to be related to the increased level of Ag–Bi disorder in the crystal structure.

Lastly, we observe an interesting reversible thermochromic behavior in HDPs $\text{Cs}_2\text{NaFeCl}_6$. Specifically, the optical bandgap of $\text{Cs}_2\text{NaFeCl}_6$ is reduced from 2.06 eV to 1.86 eV when the temperature increases from RT to 150 °C and turns back to its original value after cooling. Meanwhile, we observe lattice expansion during the heating/cooling process without phase transition. Our first-principles calculation indicates that the underlying mechanism for the thermochromic phenomenon in $\text{Cs}_2\text{NaFeCl}_6$ is mainly related to the electron-phonon coupling.

Although the development of HDPs is in its early stages, we believe that HDPs with impressive optical and electronic properties and rich substitutional chemistry have a bright future in optoelectronic and multifunctional applications. Our findings shed new light to the absorption and bandgap modulation of HDPs and provide new insights into the atomic-level structures of DPAs, which can help to develop efficient optoelectronic devices.

Keywords: Lead-free halide double perovskites, Metal doping/alloying, Bandgap engineering, Atomic-level structure, Thermochromism

Populärvetenskaplig Sammanfattning

Blyfria halid-dubbelperovskiter (HDP:er, $A_2B^{III}X_6$) med attraktiva optiska och elektroniska egenskaper betraktas som ett av de mest lovande alternativen för att övervinna de toxicitets- och stabilitetsproblem som bly-halidperovskiter för optoelektriska tillämpningar har. HDP:er ger upphov till en bredd av möjliga kombinationer och en rik möjlighet till substitutionskemi med intressanta egenskaper för olika optoelektriska komponenter. Prestandan hos vetenskapens bästa blyfria HDP:er är dock ännu inte jämförbar med bly-halidperovskiter, särskilt inte inom solcellsområdet. En av de främsta orsakerna till detta, är att HDP:er vanligtvis har stora och/eller indirekta bandgap, vilket begränsar deras optiska och optoelektroniska egenskaper i det synliga och infraröda området. I denna avhandling försöker vi modifiera bandgap och optiska egenskaper hos HDP:er med hjälp av metall-dopning/legering och kristalliseringskontroll, så väl som ge en detaljerad förståelse för legeringen på atomnivå. Vi observerar även betydande förändringar av bandgap hos HDP:er vid olika temperaturer (dvs. Termokromism) och visar på orsakerna bakom detta.

Vi antar först metall-dopning-/legeringsstrategin för att ändra absorptionsegenskaperna hos HDP-utgångsmaterialet $Cs_2AgBiBr_6$. Genom att introducera Cu som dopämne i $Cs_2AgBiBr_6$ breddar vi absorptionskanten avsevärt, från cirka 610 nm till cirka 860 nm. Systematiska karakteriseringar indikerar att Cu-dopning introducerar defekttillstånd (sub-bandgap-tillstånd) i bandgapet, utan att ändra bandgapet för $Cs_2AgBiBr_6$. Intressant nog kan dessa subbandgap generera en betydande mängd bandbärare via optisk excitation, vilket gör dessa dubbelperovskiter lovande för ljusdetektering i det nära-infraröda området.

Parallellt med materialmodifieringen med hjälp av metall-dopnings-/legeringsstrategin är den grundläggande förståelsen av dessa dopade/legerade dubbelperovskiter också av avgörande betydelse. I den andra artikeln undersöker vi atomnivåstrukturen hos dopade dubbelperovskiter genom att presentera en serie dubbelperovskitlegeringar med den kemiska formeln $Cs_2AgIn_{1-x}Fe_xCl_6$ ($x = 0-1$) som visar ett justerbart bandgap i intervallet 2.8–1.6 eV. Våra resultat visar att Fe^{3+} ersätter In^{3+} i gitteret och bildar $[FeCl_6]^{3-} \cdot [AgCl_6]^{5-}$ domäner som gradvis växer sig större när Fe^{3+} koncentrationen ökar. Det är observerat att dessa domäner kan sammanföras ytterligare för att bilda mikroskopiskt segregerade Fe^{3+} -rika faser i dubbelperovskitlegeringarna.

För att minska $\text{Cs}_2\text{AgBiBr}_6$ -HDP:ernas bandgap utvecklade vi även en kristalliseringskontrollmetod, där hög temperatur används för att främja enkristallin tillväxt. Genom att öka kristalltillväxttemperaturen från 60 °C till 150 °C kan bandgapet för $\text{Cs}_2\text{AgBiBr}_6$ minskas från 1,98 eV till 1,72 eV, vilket är det minsta bandgap som har rapporterats för $\text{Cs}_2\text{AgBiBr}_6$ i rumsförhållanden. Den underliggande orsaken antas vara relaterad till den ökade nivån av Ag-Bi-oordning i kristallstrukturen.

Slutligen har vi observerat ett intressant reversibelt termokromatiskt beteende i $\text{Cs}_2\text{NaFeCl}_6$ -HDP:er. Mer specifikt, reduceras det optiska bandgapet för $\text{Cs}_2\text{NaFeCl}_6$ från 2.06 eV till 1.86 eV när temperaturen ökar från RT till 150 °C och återgår till sitt ursprungliga värde efter kylning. Under tiden observerar vi gitterexpansion under uppvärmnings-/kylprocessen utan fasövergång. Vår första-princip-beräkning visar att den underliggande mekanismen för det termokromatiska fenomenet i $\text{Cs}_2\text{NaFeCl}_6$ främst är relaterade till elektron-fonon-koppling.

Även om utvecklingen av HDP:er är i ett tidigt skede, tror vi att HDP:er med imponerande optiska och elektroniska egenskaper och rik substitutionskemi har en ljus framtid inom optoelektroniska och multifunktionella applikationer. Våra resultat kastar nytt ljus över absorption- och bandgapmoduleringen av HDP:er och ger nya insikter gällande atomnivåstrukturer av dubbelperovskitlegeringar, vilket kan bidra till utvecklingen av effektiva optoelektroniska komponenter.

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List of Publications Included in the Thesis

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2. The Atomic-Level Structure of Bandgap Engineered Double Perovskite Alloys $\text{Cs}_2\text{AgIn}_{1-x}\text{Fe}_x\text{Cl}_6$.

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3. Lead-Free Halide Double Perovskite $\text{Cs}_2\text{AgBiBr}_6$ with Decreased Band Gap.

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4. Strong electron-phonon coupling induced thermochromism in the double perovskite $\text{Cs}_2\text{NaFeCl}_6$.

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Manuscript

Author contribution

Paper 1: Synthesized the Cu-doped $\text{Cs}_2\text{AgBiBr}_6$ single crystals, carried out most of the characterizations and data analysis, except for the photoconductivity measurement and analysis, wrote the manuscript and revised it together with co-authors.

Paper 2: Synthesized the $\text{Cs}_2\text{AgIn}_{1-x}\text{Fe}_x\text{Cl}_6$ double perovskite alloys, carried out most of the characterizations and data analysis, except for the solid-state nuclear magnetic resonance (ssNMR) measurements and analysis, wrote the manuscript and revised it together with co-authors.

Paper 3: Synthesized the $\text{Cs}_2\text{AgBiBr}_6$ single crystals, carried out most of the characterizations and data analysis, except for First-principle DFT calculations, wrote the manuscript and revised it together with co-authors.

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1. Thermochromic Lead-Free Halide Double Perovskites.

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2. Stable, High-Sensitivity and Fast-Response Photodetectors Based on Lead-Free Cs₂AgBiBr₆ Double Perovskite Films.

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Author contribution

For these papers not included in the thesis, I contributed to partial experiment preparation, characterization, and data analysis.

Abbreviations

Abbreviation	Meaning
HDPs	Halide double perovskites
3D	Three-dimensional
2D	Two-dimensional
0D	Zero-dimensional
Pb	Lead
MA	Methylammonium
FA	Formamidinium
Cs	Cesium
PCE	Power conversion efficiency
LED	Light emitting diode
EQEs	External quantum efficiency
IEC	International Electrotechnical Commission
CBM	Conduction band minimum
VBM	Valence band maximum
PL	Photoluminescence
PLQY	Photoluminescence quantum yield
STEs	Self-trapped excitons
GS	Ground state
FE	Free exciton state
FC	Free carrier state
E_g	Bandgap energy
E_b	Exciton binding energy
E_{st}	Self-trapping energy
E_d	Lattice deformation energy
E_{PL}	Emission energy
DMSO	Dimethyl sulfoxide
ETL	Electron transport layer
TiO₂	Titanium oxide
m-TiO₂	Mesoscopic titanium oxide
Spiro-OMeTAD	2,2',7,7'-tetrakis(N,N-dipmethoxyphenylamine)- 9,9'-spirobifluorene

Au	Gold
Ag	Sliver
Bi	Bismuth
Cu	Copper
Fe	Iron
Na	Sodium
In	Indium
Cl	Chlorine
Br	Bromine
ITO	Indium doped tin oxide
SnO₂	Tin oxide
NIR	Near infrared
XRD	X-ray diffraction
PXRD	Powder X-ray diffraction
SCXRD	Single-crystal diffraction
RT	Room temperature
RT-Cooling	Cooling to room temperature
SOC	Spin–orbit coupling
GBL	γ - butyrolactone
UV–Vis	Ultraviolet–visible spectrophotometry
NMR	Nuclear magnetic resonance
ssNMR	Solid-state nuclear magnetic resonance
ppm	Part per million
RF	Radiofrequency
MAS	Magic-angle spinning
PRE	Paramagnetic relaxation enhancements

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Chapter 1 Introduction

1.1 Perovskites

Perovskite originally referred to the naturally occurring calcium titanate mineral (CaTiO_3). This mineral was first discovered in Russia by Gustav Rose in 1839 and named after the Russian mineralogist Lev Perovski.^{1,2} Now, the name perovskite is generally applied to the class of compounds that have the same type of crystal structure as CaTiO_3 .² The general chemical formula for perovskite materials can be described as ABX_3 , where A and B are cations, and X is an anion. Perovskites are a large family of materials with many interesting and amazing properties, such as ferroelectricity, superconductivity, charge ordering, spin-dependent transport and high thermopower. These properties have enabled perovskites to be successfully applied in different fields, including catalysis,³ ferroelectrics,⁴ spintronics,⁵ piezoelectric⁶ and optoelectronics. In this thesis, we mainly focus on the optoelectronic applications of halide perovskites.

1.2 Crystal Structure of Perovskite

Figure 1.1a shows the unit cell of the typical ABX_3 perovskite structure. The central B-site cation bonds with six X-site anions to form BX_6 octahedron, and A-site cations stay in the corner position. These BX_6 octahedrons are connected by the corner-sharing mode to form a three-dimensional (3D) structure, where A-site cations occupy the cavities formed by four BX_6 octahedrons (**Figure 1.1 b**). Apart from the common single perovskite structure, there is another interesting perovskite structure named double perovskite structure. Double perovskite has a similar structure as single perovskite, but two different cations are ordered on B site. The general chemical formula of double perovskites can be written as $\text{A}_2\text{BB}'\text{X}_6$ (**Figure 1.1 c**). Considering a wide range of possibilities for two different B-site cations, double perovskites offer immense opportunities in terms of combinatorial chemistry.

Figure 1.1 a) Unit cell of the general perovskite. b) Schematic diagram of the structure of common single perovskite ABX_3 and double perovskite $\text{A}_2\text{BB}'\text{X}_6$.

In theory a series of compounds can satisfy the chemical formula of ABX_3 or $A_2BB'X_6$; however not all of them are stable in crystallography. There are two factors to predict the crystallographic stability of perovskites crystal structure, the Goldschmidt tolerance factor t (equation 1.1)⁷ and octahedral factor μ (equation 1.2):

$$t = \frac{(R_A + R_B)}{\sqrt{2}(R_B + R_X)} \quad (1.1)$$

$$\mu = \frac{R_B}{R_X} \quad (1.2)$$

where R_A and R_X represent the ionic radii of A and X ions. R_B is the radii of B cation in single perovskite and refers to the average radius of B and B' cations in double perovskite. To form a stable perovskite structure, the Goldschmidt tolerance factor t and octahedral factor μ are usually in the range of $0.81 < t < 1.11$ and $0.41 < \mu < 0.90$, respectively.^{8,9} When the tolerance factor t is equal to 1.0, it will form an ideal symmetrical cubic crystal structure with high stability, such as $SrTiO_3$. Perovskites usually maintain the major cubic structure when the tolerance factor t is between 0.9 and 1.0. When t is reduced to the range of 0.89 to 0.81, the cubic crystal structure would possibly be distorted into an orthorhombic or rhombohedral structure. If t is further decreased, the crystal cannot retain the perovskite structure. When $t > 1.0$, a hexagonal or tetragonal structure is most likely to form. Besides the consideration of t , the value of octahedral factor μ should be between 0.41 and 0.90 for the formation of a stable BX_6 octahedra.⁹ Both the tolerance factor t and octahedral μ are necessary to predict the stability of perovskite structure.

1.3 Lead Halide Perovskites

Lead (Pb) halide perovskites with the formula of $APbX_3$ is one of the most famous perovskite materials, where A is the organic cation methylammonium (MA^+), formamidinium (FA^+) or inorganic cation cesium (Cs^+), and X is the halogen anion Cl^- , Br^- or I^- . As a new generation of semiconductors, Pb halide perovskites have achieved great success in various optoelectronic applications.

1.3.1 Applications of Lead Halide Perovskites

One of the most successful applications of Pb halide perovskite is solar cells.¹⁰ The first perovskite solar cells was fabricated by Miyasaka and colleagues in 2009 and achieved a power conversion efficiency (PCE) of 3.8%.¹⁰ In 2012, Snaith and coworkers first adopted the solid-state perovskite solar cell structure and enhanced the PCE to 10.9%.¹¹ After that, halide perovskites have achieved significant breakthroughs, with the PCE of 25.5% now,¹² which has surpassed commercial polycrystalline silicon solar cells and is

comparable to the monocrystalline silicon solar cells. The excellent performance is mainly due to their superior optoelectronic properties, such as suitable and tunable direct band gap, high absorption coefficient, balanced and small carrier effective masses, long carrier lifetime and diffusion length, small exciton binding energy and high defect tolerance (**Figure 1.2**).^{11,13–17}

Figure 1.2 Advantages and optoelectronic applications of lead halide perovskites.

In contrast to solar cell devices, Pb halide perovskites can also convert electricity into light by light emitting diode (LED) devices. The room temperature perovskite LED was first reported by R. H. Friend and coworkers in 2014 and achieved an external quantum efficiency (EQEs) of 0.76%.¹⁸ Since then, many effects have been focused on this direction, and the EQEs of perovskite LEDs have increased dramatically. Up to now, the EQEs of green, red and near-infrared perovskite LEDs have been improved to more than 20%.^{19–21} Even for the more challenging blue perovskite LEDs, the best EQE has reached 12.3%.²²

In addition to the successful application of Pb halide perovskite in solar cells and LEDs, its unique and remarkable optoelectronic properties make it also employed in other optoelectronic applications, such as photodetectors,²³ lasers,²⁴ transistors,²⁵ X-ray detectors,²⁶ thermoelectrics,²⁷ and memory devices (**Figure 1.2**).²⁸

1.3.2 Challenges and Solutions

Although Pb-based perovskites have achieved great success in optoelectronics field, the issues of poor stability and toxic Pb hinder their further development. In this section, we

identify challenges in Pb-based perovskites and discuss possible solutions: improving its stability and solving the toxicity of Pb.

Stability is a key concern for the commercialization of perovskite photoelectric devices. Unfortunately, Pb halide perovskites are chemically unstable after exposure to light, oxygen, moisture, and heat.²⁹ Different factors degrade perovskite materials in different mechanisms, such as polymorphic transformation, hydration and decomposition (**Figure 1.3**).³⁰ It is also highly dependent on the specific perovskite composition. For example, MAPbI₃ is the most famous and popularly studied hybrid Pb halide perovskite, which is easily decomposed into PbI₂ and MAI under a humid environment. This is because water molecules can easily form strong hydrogen bonds with organic cation (MA⁺) and weaken the hydrogen-bonding interaction between organic cation and PbX₆ octahedra, causing the degradation of perovskite.³¹ Meanwhile, the MAPbI₃ perovskite cannot withstand at high temperature (140 °C) and can be decomposed into PbI₂ even at 85 °C for a long time,³² which is highly related to the volatile organic compound MA⁺. Other effects such as irradiation and oxygen can also cause the decomposition of perovskite materials. In addition, the formation enthalpy of MAPbI₃ measured by Navrotsky and coworkers is positive, implying that MAPbI₃ is thermodynamically unstable and prone to decomposition even without external influences.³³

Figure 1.3 Schematic illustration of the environmental factors and mechanisms that are responsible for the degradation of emerging perovskites.³⁰

The stability can be enhanced by substituting organic cations with inorganic cations such as Cs⁺, which could result in an intrinsic or thermodynamic stable compound. Correspondingly, the all-inorganic perovskite CsPbI₃ shows improved tolerance to oxygen and heat than MAPbI₃. However, it has a poor phase stability. The perovskite phase (‘black’ phase) of CsPbI₃ would easily transform to the nonperovskite phase (‘yellow’ phase) that is thermodynamically more stable at room temperature.³⁴ This is possibly originating from the relatively low tolerance factor t ($t < 0.8$) of CsPbI₃, making CsPbI₃

tend to form the nonperovskite orthorhombic phase ('yellow' phase). It is noted that this stable 'yellow' phase has poor absorption and low carrier mobility, which is not suitable for photoelectronic applications. Therefore, phase stability is also very important and needs to be considered before utilizing these inorganic halide perovskites.

To stabilize the perovskite phase of CsPbI_3 , one approach is to increase its Goldschmidt tolerance factor t by incorporating larger A-site cations. Since Cs^+ is already the largest nonradioactive Group-I element, larger organic cations (such as MA^+ and FA^+) become the only suitable choice for A-site doping. However, there is a tradeoff between phase stability and environmental stability regarding the ratio of inorganic and organic cations. Another approach is to replace I^- by a part of the smaller-size Br^- with the formation of alloyed perovskites, which could increase the tolerance factor t and retain the all-inorganic composition, as indicated by some reports.³⁵ Meanwhile, Br^- alloying can enlarge the bandgap, and thus making final perovskites suitable for tandem solar cells. A critical issue for these alloys is the segregation of halides during devices operation, which could cause emission color instability issues in LED devices.

In addition to the instability of perovskites, the presence of toxic Pb is another concern for practical applications. In the case of encapsulant failure, the leakage of Pb would cause damage to human health and the environment. As shown in **Figure 1.4**, when accidental exposed to Pb, the human body possibly ingests Pb through the gastrointestinal, respiratory, and dermal. Meanwhile, the blood can transport the Pb ions to various organs of the human body, and eventually the skeleton is the major depository for Pb in the body. Pb compounds could interfere with heme activity and cause damage to our renal, reproductive, and central nervous systems. Finally, Pb resides in all of the three compartments with a certain organ-specific retention time, after which it is excreted from the body through urine, gastrointestinal secretion, hair, sweat, nails and breast milk (**Figure 1.4**).³⁶ In addition to toxic Pb, several other ways such as acidification and nanotoxicity of perovskite materials are also potentially harmful to the environment and human health.^{36,37}

Figure 1.4 Schematic overview of absorption, distribution, and excretion of Pb compounds in the human body. For each route of intakes, a percentage indicates the overall amount that can be absorbed. Pb not absorbed upon gastrointestinal intake leaves the body via the faeces (as indicated); Pb not absorbed by respiratory or dermal routes is assumed to have left the body directly by exhalation or to have lost contact through natural body movement, respectively (not indicated in the figure).³⁶

Device encapsulation is an effective approach to address the toxicity and instability issues of Pb halide perovskites, as it can isolate the perovskites materials from oxygen and moisture and can effectively avoid the leakage of toxic Pb. It has found that the polymer/glass stack encapsulation can make Pb halide perovskite solar cells pass the International Electrotechnical Commission (IEC) 61215:2016 photovoltaic module standard tests.³⁸ Even though encapsulation can suppress the decomposition of perovskites, the fundamental instability and toxicity of hybrid Pb halide perovskites are not resolved.

Comparing with device encapsulation, the straightforward approach for the toxicity issue is to replace the toxic Pb^{2+} with other low-toxic or non-toxic elements. Sn^{2+} and Ge^{2+} are natural substitution candidates with the formation of similar three-dimensional structure as Pb-based perovskite, because they are in the same group as Pb^{2+} in the periodic table. As expected, these materials have achieved a relatively high PCE than other alternatives. However, both Sn^{2+} and Ge^{2+} are easily oxidized to their tetravalent state, resulting in the instability of these perovskite materials.^{39,40} In contrast, heterovalent cations such as In^{3+} , Bi^{3+} , Sb^{3+} , Ti^{4+} , Pd^{4+} , and Eu^{3+} are relatively stable, which provide more possibilities for searching nontoxic and stable candidates.⁴¹⁻⁴⁵ Unfortunately, to maintain the charge neutrality, the chemical formulas of these new compounds have

changed significantly compared to APbX_3 perovskites. Correspondingly, their crystal structures have become a low-dimensional structure to accommodate heterovalent substitution, including zero-dimensional (0D)^{41,42,46} and two-dimensional (2D).^{47–51} Therefore, we consider these new lead-free materials as perovskite derivatives. Although these derivatives are nontoxicity and relatively stable in ambient environment, they exhibit indirect bandgaps, poor carrier transport, deep defects, and high exciton binding energies due to their low structural and electronic dimensionality, which hinder their applications in optoelectronic field. It is highly desirable to explore new lead-free candidates with high structure and electronic dimensionality.

Chapter 2 Lead-free Halide Perovskites

2.1 Three-Dimensional Lead-Free Halide Perovskites

One critical parameter for promising lead-free perovskite candidates is 3D crystal structure with high electronic dimensionality. To meet this requirement, the candidates should have suitable Goldschmidt tolerance factor t and octahedral factor μ to form a stable 3D crystal structure. Meanwhile, the B-site cation should be bivalent (+2) to keep electrical neutrality for metal halide perovskite ABX_3 , as the A-site cation is monovalent (+1) and the anion X is negatively monovalent (−1). Another feasible and attractive approach is the combination of $B^+(B^I)$ and $B^{3+}(B^{III})$ cations to replace two B^{2+} , forming a 3D double perovskite. While a special kind of compounds formed by replacing two B^{2+} cations with a B^{4+} and a vacancy was previously described as quasi-3D vacancy ordered double perovskites, it is more appropriate to view these $A_2B^{4+}X_6$ -type compounds as 0D perovskite derivatives considering that their octahedrons are completely isolated. Therefore, strictly speaking, there are mainly two types of 3D Pb-free perovskites, $AB^{2+}X_3$ and $A_2B^IB^{III}X_6$.

$ASn^{2+}X_3$ and $AGe^{2+}X_3$ based 3D $AB^{2+}X_3$ -type Pb-free perovskites have been discussed in Section 1.3.2. A big disadvantage of these materials is their poor stability issues since Sn^{2+} and Ge^{2+} are easily oxidized to Sn^{4+} and Ge^{4+} . Here, I will focus on halide double perovskites (HDPs) $A_2B^IB^{III}X_6$, which are considered as the most promising candidates for stable 3D Pb-free perovskites.

2.2 Three-Dimensional Lead-Free Halide Double Perovskites

The typical ordered halide double perovskite structure contains alternating $[B^IX_6]^{5-}$ and $[B^{III}X_6]^{3-}$ octahedra, and A site cations are in the cavities formed by octahedrons (**Figure 2.1a**). The alternating arrangement of $[B^IX_6]^{5-}$ and $[B^{III}X_6]^{3-}$ octahedra in the 3D structure is termed rock-salt ordering. As I have just highlighted, a big advantage of double perovskite is their similar 3D structure to that of the common single perovskite. Besides, double perovskites allow more kinds of cations to be incorporated into the B^I/B^{III} sites, which could enable access to an expansive range of alternative components. Feliciano Giustino and Henry J. Snaith highlighted the elements in the periodic table which belong to halide double perovskites, as shown in **Figure 2.1b**. The numbers of elements that can be occupied in A^+ , B^I , B^{III} and X^- sites are 7, 8, 34 and 5, respectively. By simply multiplying these numbers together, we can obtain around 9520 compounds without considering the phase stability.⁵² Even though the majority of these compounds are unstable due to their unsuitable octahedral factor μ , it is believed that there are still more than 600 structurally stable compounds that have never been exploited.⁵²

The first reported double perovskite, K_2NaAlF_6 , formerly known as elpasolites, was discovered in El Paso County, Colorado in 1883. When the time came to 2016, three groups reported the new double perovskites Cs_2AgBiX_6 ($X=Br, Cl$) with exciting optoelectronic properties,^{53–55} which stimulates the research interest into these HDPs for potential photovoltaic applications. Since then, an increasing number of new halide double perovskites have been synthesized, such as $Cs_2AgInCl_6$,⁵⁶ Cs_2AgTiX_6 ($X=Br, Cl$),^{57,58} $Cs_2AgSbCl_6$ ⁵⁹ and $Cs_2AgFeCl_6$,⁶⁰ etc.

Figure 2.1 (a) Schematic view of B^{1+}/B^{3+} cation substitution from halide perovskites ($AB^{2+}X_3$) to double perovskites ($A_2B^{1+}B^{3+}X_6$). (b) Composition available for lead-free double perovskites ($A_2B^{1+}B^{3+}X_6$). The triangular tags with different colors specify the site occupied by the element, illustrated as the legend at the top-middle site.⁵²

2.2.1 Basic Properties

Up to now, $Cs_2AgBiBr_6$ and $Cs_2AgInCl_6$ are the most famous and widely studied double perovskites. $Cs_2AgBiBr_6$ crystallizes as red truncated octahedra in cubic space group $Fm\bar{3}m$ (No. 225) at room temperature (Figure 2.2f inset) and can be easily synthesized by the hydrothermal method. As shown in **Figure 2.2a,b**, its conduction band minimum (CBM) is mainly derived from Bi 6p–Br 4p antibonding states, and the valence band

maximum (VBM) is mainly derived from Ag 4d–Br 4p antibonding states. Since the CBM is located at the *L* point and VBM is located at X point, Cs₂AgBiBr₆ shows an indirect bandgap.⁶¹ Based on the UV-Vis absorption spectrum, the calculated indirect optical bandgap of Cs₂AgBiBr₆ is in the range of 1.95–2.19 eV (**Figure 2.2c**).^{53,54}

Figure 2.2 (a) Band structures and (b) total and projected densities of states (DOSs) of Cs₂AgBiBr₆ calculated with the HSE+SOC methods.⁶¹ (c) Absorbance spectrum of Cs₂AgBiBr₆ powder. Inset: Tauc plot showing the characteristics of an indirect band gap.⁵³ (d) Steady-state room-temperature photoluminescence (PL) spectrum of a powdered Cs₂AgBiBr₆ sample upon 500 nm excitation. Inset: low-temperature PL spectrum.⁵³ (e) PL intensity as a function of carrier density. The PL intensities were the values just after photoexcitation (PL|_{t=0}), rather than the integrated PL intensity.¹⁴ (f) Time-resolved room-temperature PL and fits for the PL decay time (τ) in powder and single-crystal samples. Inset: Photograph of a single crystal of Cs₂AgBiBr₆.⁵³

The photoluminescence (PL) peak of Cs₂AgBiBr₆ centered at 1.87 eV at room temperature and centered at 1.98 eV at 22.6 K (**Figure 2.2d**).⁵³ The measured PL quantum yield (PLQY) of Cs₂AgBiBr₆ is only around 0.08%, since the radiative recombination in indirect bandgap materials requires phonon assistance. Besides, the coexistence of excitons and free carriers in Cs₂AgBiBr₆ was revealed by Tze Chien Sum and co-workers through measuring PL density in terms of different excitation intensities (**Figure 2.2e**).¹⁴ Interestingly, the carrier lifetimes of Cs₂AgBiBr₆ can be as long as 668 ns (**Figure 2.2f**) or even more than 1 μ s,^{53,62} which could be related to its indirect bandgap. Meanwhile, our group demonstrated that the high quality Cs₂AgBiBr₆ films have a long carrier diffusion length greater than 100 nm.¹⁴ Naomi S. Ginsberg and co-workers reported that the carrier diffusion length in Cs₂AgBiBr₆ crystal can even exceed 1 μ m.⁶³

Moreover, $\text{Cs}_2\text{AgBiBr}_6$ possesses relatively low carrier effective masses which are favorable for efficient charge transport and extraction.

More attractively, HDPs usually show excellent moisture, light, and thermal stability. For example, there was no decomposition for $\text{Cs}_2\text{AgBiBr}_6$ after storing under 55% humidity for 30 days or irradiating it with a white LED lamp (0.75 Sun) under N_2 for one month (**Figure 2.3a**). Meanwhile, the decomposition temperature of $\text{Cs}_2\text{AgBiBr}_6$ is higher than 500°C (**Figure 2.3b**).⁶⁴ These excellent chemical and thermal stability make $\text{Cs}_2\text{AgBiBr}_6$ double perovskite a promising candidate for stable photovoltaic applications.

Figure 2.3 (a) PXRD patterns of $\text{Cs}_2\text{AgBiBr}_6$ after exposure to humidity (55% RH) or light (0.75 Sun) for 30 days. Asterisks denote signals from the sample holder.⁵³ (b) Thermogravimetric analysis (TGA) of $\text{Cs}_2\text{AgBiBr}_6$ double perovskite.⁶⁴

Another interesting halide double perovskite is $\text{Cs}_2\text{AgInCl}_6$, which crystallizes in a cubic unit cell with the same space group $Fm\bar{3}m$ as $\text{Cs}_2\text{AgBiBr}_6$. $\text{Cs}_2\text{AgInCl}_6$ has a typical double perovskite structure consisting of alternating $[\text{AgCl}_6]^{5-}$ and $[\text{InCl}_6]^{3-}$ octahedra in all three directions. In 2018, Tang and co-workers grow high-quality $\text{Cs}_2\text{AgInCl}_6$ single crystals with extremely low trap density, $(8.6 \pm 1.9) \times 10^8 \text{ cm}^{-3}$, by employed the hydrothermal method. The carrier mobility of the resulted $\text{Cs}_2\text{AgInCl}_6$ can up to $3.31 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁶⁵ It is noted that $\text{Cs}_2\text{AgInCl}_6$ has a direct band gap with both the CBM and VBM located at the Γ point, as shown in **Figure 2.4a**. However, the transitions from VBM to CBM at the Γ point are parity forbidden (**Figure 2.4a,c**), as VBM and CBM have the same even parity, where the CBM mainly derives from the delocalized In 5s states and the VBM mainly derives from Ag 4d and Cl 3p states.⁶⁶ Therefore, $\text{Cs}_2\text{AgInCl}_6$ should have a weak optical absorption coefficient near the band edge. The optical transitions gradually become allowed as the k point changes from Γ to L point due to the introduce of odd character, which is evident in the calculated dipole transition matrix element (**Figure 2.4b**).

Figure 2.4 PBE calculated (a) band structure and (b) transition matrix elements for Cs₂AgInCl₆. The orange color corresponds to Cl 3p states, the green color to In 5s states, and the blue/cyan color to Ag 4d/5s states.⁶⁶ (c) Band diagram depicting allowed and forbidden optical transitions.⁶⁵

The optical properties of Cs₂AgInCl₆ have been widely investigated by UV-vis and PL spectra. UV-Vis absorption spectra shows two absorption edges with a sharp absorption near 384 nm (3.2 eV) and a weak absorption near 595 nm (2.1 eV) (**Figure 2.5a**).⁶⁵ The calculated optical bandgap of Cs₂AgInCl₆ is in the range of 2.8 eV -3.3 eV.^{67,68,56} The different bandgap values are possibly related to the different forms of the measured samples (powder or crystal). It is noted that Cs₂AgInCl₆ shows a broad PL peak centered at around 2.0 eV with a large Stokes shift compared with its fundamental bandgap (**Figure 2.5b**). It also shows an extremely low PLQY (< 0.1), which is mainly related to its self-trapped excitons (STEs) luminescence. Specifically, STEs in Cs₂AgInCl₆ should arise from the strong Jahn-Teller distortion of the AgCl₆ octahedron in the excited state, indicated by first-principles density-functional-theory calculations (**Figure 2.5d**).⁶⁸ The energy difference between STE emission and bandgap relates with the exciton binding energy E_b , the self-trap energy E_{st} and the lattice deformation energy E_d (**Figure 2.5c**). For Cs₂AgInCl₆, there is another small PL peak located at 425 nm, possibly from the free-exciton emission. The PL lifetime of Cs₂AgInCl₆ at 595nm (566.9 ns) is much longer than that at 425nm (9.8 ns). The parity-forbidden transitions from CBM to VBM, together with STEs, cause the relatively long lifetime at 595nm and low PLQY (< 0.1).

Figure 2.5 (a) Absorption spectrum of $\text{Cs}_2\text{AgInCl}_6$ single crystals. Weak absorption was observed around 595 nm. Inset: Tauc plot showing the characteristics of a direct band gap of 3.2 eV (384 nm).⁶⁵ (b) Calculated photoluminescence spectrum compared with the experimental result. The calculated curve has been shifted to align its maximum with that of the experimentally measured curve for better comparison.⁶⁸ (c) Schematic of the energy level structure of STE (GS, ground state; FE, free exciton state; FC, free carrier state; STE, self-trapped exciton state; E_g , bandgap energy; E_b , exciton binding energy; E_{st} , self-trapping energy; E_d , lattice deformation energy; E_{PL} , emission energy).⁶⁹ (d) STE in $\text{Cs}_2\text{AgInCl}_6$. Cs atoms are omitted for clarity. The cyan and magenta isosurfaces represent the electron and hole orbital densities, respectively. The electron state (red dashed circle) is rather extended and the hole state (black dashed circle) is compact, consistent with the small (large) effective mass of the conduction (valence) band. The inset shows the Jahn–Teller distortion of the AgCl_6 octahedron. Here the hole isosurface is obvious, whereas the electron isosurface is invisible owing to its small density.⁶⁸

$\text{Cs}_2\text{AgInCl}_6$ also shows excellent chemical, light, and thermal stability. There is no decomposition in the PXRD patterns after storing $\text{Cs}_2\text{AgInCl}_6$ either in the dark at 55% relative humidity for 300 days or irradiated at 50 °C with an LED lamp at an intensity of 5.02 mW/cm^{−2} for 48h, as shown in **Figure 2.6 a,b**. Meanwhile, $\text{Cs}_2\text{AgInCl}_6$ exhibits high thermal stability without phase transition before the decomposition temperature of around 507 °C. (**Figure 2.6c**).⁶⁵

Figure 2.6 (a) PXRD patterns of $\text{Cs}_2\text{AgInCl}_6$ powder after exposure to humidity (55% RH).⁶⁵ (b) PXRD patterns of $\text{Cs}_2\text{AgInCl}_6$ powder after exposure to light ($5.02 \text{ mW}/\text{cm}^2$).⁶⁵ (c) Thermogravimetric differential thermal analysis of $\text{Cs}_2\text{AgInCl}_6$ powder.⁶⁵

In addition to the benchmark double perovskites $\text{Cs}_2\text{AgBiBr}_6$ and $\text{Cs}_2\text{AgInCl}_6$, researchers are committed to exploring other new promising HDPs for efficient photovoltaic applications. Hemamala I. Karunadasa and co-workers synthesized TI-based double perovskites $\text{Cs}_2\text{AgTiX}_6$ ($X = \text{Br}, \text{Cl}$) for the first time.⁵⁸ Impressively, $\text{Cs}_2\text{AgTiBr}_6$ shows a direct bandgap with the lowest bandgap (0.95 eV) amongst reported halide perovskites (**Figure 2.7a**). Unfortunately, there is no PL in $\text{Cs}_2\text{AgTiBr}_6$ and $\text{Cs}_2\text{AgTiCl}_6$ even at 20K, mainly because of the symmetry-forbidden transition. Recently, Li and co-workers investigated a new class double perovskite $\text{Cs}_2\text{AgIn}_x\text{Fe}_{1-x}\text{Cl}_6$ ($0 \leq x \leq 1$) with a broadband absorbance in the range of 450–800 nm, as shown in **Figure 2.7b**. Among these different compositions, $\text{Cs}_2\text{AgFeCl}_6$ shows a direct bandgap of around 1.55 eV, but it displays no PL.⁶⁰ The underlying reasons were explained by lacking of electronic transitions occur to maintain the radiative recombination of electric charges, as the valance electrons originating from the $\text{Cs}_2\text{AgFeCl}_6$ are more likely to undergo the bound transition state. Additionally, a series of Na-based double perovskites have been studied by Xia's group. For example, $\text{Cs}_2\text{NaBi}_{1-x}\text{In}_x\text{Cl}_6$ exhibit relatively large bandgap, ranging from 3.41 eV to 3.7 eV, as shown in **Figure 2.7c**.⁷⁰ Although a range of different HDPs have been investigated, we believe that there is still a huge room for further exploration of new double perovskites with interesting properties.

Figure 2.7 (a) Absorption spectra of Cs₂AgTlBr₆ and Cs₂AgTlCl₆ (solid lines) and those of Cs₂AgBiBr₆ and Cs₂AgBiCl₆ (dashed lines).⁵⁸ (b) UV-vis absorbance spectra of as-prepared Cs₂AgFe_{1-x}In_xCl₆ (0 ≤ x ≤ 1) double perovskite single crystals with different x values.⁶⁰ (c) Tauc plots for Cs₂NaBi_{1-x}In_xCl₆ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.7, 0.9, and 1.0).⁷⁰

2.2.2 Applications of Lead-free Halide Double Perovskites

Encouraged by the interesting optoelectronic properties of HDPs, these materials are attractive for practical optoelectronic applications, such as solar cells,⁷¹ laser,⁷² light emitting diode (LED),⁶⁸ photodetector,⁷³ X-ray detector and imaging,⁷⁴ photocatalyst,⁷⁵ etc. (Figure 2.8).

The early applications of HDPs are limited to single crystals, as it is difficult to develop double perovskite films using the solution method. For example, Tang and co-workers demonstrated a sensitive (detectivity of $\sim 10^{12}$ Jones), stable and fast (3 dB bandwidth of 1035 Hz) UV photodetectors based on the Cs₂AgInCl₆ single crystals.⁶⁵ Besides, Cs₂AgBiBr₆ has also been used to detect photons and even high-energy radiation, such as X-rays and γ-rays. Due to the high average atomic number, adequate $\mu\tau$ product, low ionization energy and high resistivity of Cs₂AgBiBr₆ single crystals, the fabricated X-ray detector shows a high sensitivity of $105 \mu\text{C Gy}_{\text{air}}^{-1} \text{cm}^{-2}$ and a low detection limit of $59.7 \text{ nGy}_{\text{air}} \text{s}^{-1}$ under an external bias of 5 V.⁷⁴

Figure 2.8 Optoelectronic Applications of Halide Double Perovskites.⁷⁶

The breakthrough for double perovskite films was made in 2017 by Bein and co-workers. They resolved the solubility issue of $\text{Cs}_2\text{AgBiBr}_6$ through choosing dimethyl sulfoxide (DMSO) as solvent and heating the precursor solution at 75 °C. As such, they have been able to deposit $\text{Cs}_2\text{AgBiBr}_6$ films by the spin-coating method for the first time.⁷¹ Based on the prepared films, they developed the $\text{Cs}_2\text{AgBiBr}_6$ -based solar cells with traditional mesoporous structure and achieved a PCE of 2.43%.⁷¹ They also emphasized that the high annealing temperature (250 °C) is important for obtaining pure $\text{Cs}_2\text{AgBiBr}_6$ double perovskite phase. The successful preparation of the $\text{Cs}_2\text{AgBiBr}_6$ thin films broke the main barrier of double perovskite materials for photovoltaic solar cell applications. Thereafter, different methods have been applied to fabricate the $\text{Cs}_2\text{AgBiBr}_6$ based solar cells, such as antisolvent dropping technology,⁷⁷ low-pressure-assisted method,⁷⁸ and sequential vapor deposition.⁷⁹ **Table 2.1** summarizes the device photovoltaic performance of $\text{Cs}_2\text{AgBiBr}_6$ based solar cells. Our group fabricated the $\text{Cs}_2\text{AgBiBr}_6$ solar cells with planar structure for the first time and achieve a PCE of 1.22% in 2018.¹⁴ Particularly, we achieved a uniform and high quality $\text{Cs}_2\text{AgBiBr}_6$ film by using single crystal $\text{Cs}_2\text{AgBiBr}_6$ precursor solution and one-step spin-coating method. Very recently, some researchers have enhanced the PCE of $\text{Cs}_2\text{AgBiBr}_6$ solar cells

through optimizing the electron transport layer (ETL). For example, Yang and co-workers developed a multifunctional ETL ($\text{Ti}_3\text{C}_2\text{T}_x@\text{TiO}_2$) to improve the efficiency and stability of $\text{Cs}_2\text{AgBiBr}_6$ solar cells compared to the device based on TiO_2 .⁸⁰ Wang and co-workers demonstrated a state-of-the-art PCE of 3.11% by introducing a carboxy-chlorophyll derivative (C-Chl)-sensitized mesoporous TiO_2 (m- TiO_2) film as an ETL, which could enhance the optical absorption of device, and increase short-circuit current density from 3.22 to 4.09 mA cm^{-2} .⁸¹ In all, $\text{Cs}_2\text{AgBiBr}_6$ solar cells usually exhibit excellent stability under ambient environment, but the PCE still needs to be improved.

Table 2.1 Device architecture and photovoltaic parameters of double perovskite-based solar cells.

Device structure	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF	PCE [%]	Methods	Ref.
FTO/ TiO_2 /m- TiO_2 / $\text{Cs}_2\text{AgBiBr}_6$ /Spiro- OMeTAD/Au	3.93	0.98	0.63	2.43	One-step spin coating	⁷¹
ITO/Cu- NiO/ $\text{Cs}_2\text{AgBiBr}_6$ /C60/ BCP/Ag	3.19	1.01	0.69	2.23	Antisolvent dropping	⁷⁷
ITO/ SnO_2 / $\text{Cs}_2\text{AgBiBr}_6$ / P3HT/Au	1.78	1.04	0.78	1.44	Low-pres- sure-assisted	⁷⁸
ITO/ SnO_2 / $\text{Cs}_2\text{AgBiBr}_6$ /Au	1.5	0.95	0.6	0.86	Low-pres- sure-assisted	⁷⁸
FTO/ TiO_2 / $\text{Cs}_2\text{AgBiBr}_6$ / P3HT/Au	1.79	1.12	0.68	1.37	Sequential vapor deposi- tion	⁷⁹
ITO/ TiO_2 / $\text{Cs}_2\text{AgBiBr}_6$ / Spiro-OMeTAD/Au	1.55	1.06	0.74	1.22	One-step spin coating	¹⁴
FTO/ $\text{Ti}_3\text{C}_2\text{T}_x@\text{TiO}_2$ (0.2 wt %)/ $\text{Cs}_2\text{AgBiBr}_6$ /Spiro- OMeTAD/ MoO_3 /Ag	4.14	0.96	0.70	2.81	One-step spin coating	⁸⁰
FTO/ TiO_2 / C-Chl m- TiO_2 / $\text{Cs}_2\text{AgBiBr}_6$ /Spiro- OMeTAD /Ag	4.09	1.04	0.73	3.11	One-step spin coating	⁸¹

The benchmark HDPs for potential light emitting applications is $\text{Cs}_2\text{AgInCl}_6$ with a direct bandgap. As mentioned above, $\text{Cs}_2\text{AgInCl}_6$ shows an extremely low PLQY (< 0.1)

due to the parity-forbidden transitions, which is a disadvantage for light emitting applications. Attractively, Tang and co-workers break the parity-forbidden transitions of $\text{Cs}_2\text{AgInCl}_6$ by Na alloying. The photoluminescence efficiency of Na-alloyed $\text{Cs}_2\text{AgInCl}_6$ has increased by three orders of magnitude compared to pure $\text{Cs}_2\text{AgInCl}_6$. Further introducing a trace amount of Bi^{3+} doping, the PLQY of $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ is up to $(86 \pm 5)\%$, which represents the highest reported value for white-emitting phosphors (**Figure 2.9a**). Meanwhile, the alloyed $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ also exhibited outstanding stability, indicating promise for solid-state lighting. Moreover, they also successfully fabricated a pure phase $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ film for LED devices through thermally evaporate method (**Figure 2.9b,c,d**).⁶⁸ This work demonstrated the great potential of HDPs for LED applications, although further optimization is still needed to improve device performance.

Figure 2.9 (a) Activation energy and PLQY of $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$ powder versus Na content.⁶⁸ (b) The electroluminescent device structure, glass/ PEIE modified ITO /PEIE modified ZnO (20 nm) / $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$ film(50 nm)/ TAPC(40 nm)/ MoO_3 (8 nm)/ Al(100 nm), where PEIE is polyethylenimine, TAPC is 4,4'-Cyclohexylidenebis[N,N-bis(4-methylphenyl) benzenamine].⁶⁸ (c) Electroluminescence spectra at an applied voltage of 11 V, 12 V, 13 V and 14 V, respectively. The inset is the normalized spectra.⁶⁸ (d) Dependence of current density and luminance on the driving voltage.⁶⁸

Apart from Na^+ alloying, a series of dopants has been used to change the PL emission of $\text{Cs}_2\text{AgInCl}_6$, such as Mn^{2+} , Bi^{3+} and rare earth elements (Yb^{3+} , Er^{3+}).^{82–84} In the Mn-doped $\text{Cs}_2\text{AgInCl}_6$ system, the photoexcited host ($\text{Cs}_2\text{AgInCl}_6$) transfers the energy to

Mn ions, resulting in a red colored emission at around 632 nm. Generally, the photoluminescent mechanism in Mn-doped materials originates from the de-excitation of Mn d electrons from the 4T_1 to 6A_1 state.⁸² Recently, Nag and co-workers developed a Bi^{3+} - Ln^{3+} ($\text{Ln} = \text{Er}^{3+}$ and Yb^{3+}) co-doping system to achieve efficient near-infrared PL in $\text{Cs}_2\text{AgInCl}_6$. Upon excitation, the absorption energy can be efficiently transferred to Er^{3+} and Yb^{3+} f electrons, and then de-excite by emitting light at 1540 and 994 nm, respectively.⁸⁴ Impressively, Bi^{3+} co-doping significantly promoted the near infrared (NIR) dopant emissions by creating a new absorption channel in 350–400 nm range. This co-doping strategy also provide a possibility of using doped double perovskites in infrared detection.

In addition, there are some other optoelectronic applications for halide double perovskites, such as lasers and photocatalysts, as shown in **Figure 2.8**. For instance, many fluoride double perovskites have been used as a host for Ce^{3+} -based laser materials for a long time.⁷² In 2018, Su and co-workers have demonstrated the photocatalytic application of $\text{Cs}_2\text{AgBiBr}_6$ nanocrystals for the first time. These $\text{Cs}_2\text{AgBiBr}_6$ nanocrystals were used to artificial photochemical conversion of the CO_2 into sustainable solar fuels (CO , CH_4) with an impressive electron consumption of $105 \mu\text{mol g}^{-1}$ (6 h), which holds a great potential in further photochemical applications.⁷⁵

2.3 Challenges

HDPs provide a wide range of possible combinations and rich substitutional chemistry with attractive optical and electronic features. They are promising to overcome the toxicity and instability issues of Pb halide perovskites for optoelectronic applications.

Up to now, a range of halide double perovskites have been synthesized, such as $\text{Cs}_2\text{AgBiBr}_6$, $\text{Cs}_2\text{AgBiCl}_6$, $\text{Cs}_2\text{AgSbCl}_6$, $\text{Cs}_2\text{AgInCl}_6$, $\text{Cs}_2\text{NaInCl}_6$, $\text{Cs}_2\text{NaBiCl}_6$, $\text{Cs}_2\text{NaFeCl}_6$,⁸⁵ $\text{Cs}_2\text{AgFeCl}_6$ and $\text{Cs}_2\text{NaVCl}_6$.⁸⁶ However, there are still some challenges for the optoelectronic applications. For example, the Fe-based double perovskite $\text{Cs}_2\text{AgFeCl}_6$ with a relatively narrow direct band gap of about 1.55 eV shows no PL emission. Similarly, no PL signal can be observed in $\text{Cs}_2\text{AgTlX}_6$ ($\text{X} = \text{Br}$, Cl) even at extremely low temperature (20 K). The non-luminescent behavior of these HDPs limit their optoelectronic applications. In addition, the high toxicity of Tl-based double perovskites must be considered for any applications. Na-based double perovskites show relatively large band gaps with the value of 3.41 eV and 3.70 eV for $\text{Cs}_2\text{NaBiCl}_6$ and $\text{Cs}_2\text{NaInCl}_6$, which are not ideal for photovoltaic applications either.⁷⁰

Currently, the most promising HDPs for photoelectronic applications are two benchmark double perovskites $\text{Cs}_2\text{AgBiBr}_6$ and $\text{Cs}_2\text{AgInCl}_6$. However, the bandgap of both

$\text{Cs}_2\text{AgBiBr}_6$ (> 1.95 eV) and $\text{Cs}_2\text{AgInCl}_6$ (>2.8 eV) are too large for single junction photovoltaic applications. The large bandgap results in low absorption in the visible-light region, limiting their photovoltaic performance. To date, the highest reported PCE of $\text{Cs}_2\text{AgBiBr}_6$ double perovskite solar cells is only 3.11%. For $\text{Cs}_2\text{AgInCl}_6$ with a direct bandgap, it suffers from an unfavorable parity-forbidden transitions from CBM to VBM. Meanwhile, it is still challenging to fabricate $\text{Cs}_2\text{AgInCl}_6$ films by the solution method due to the low solubility of CsCl and AgCl.

In short, apart from the benchmark double perovskites $\text{Cs}_2\text{AgInCl}_6$ and $\text{Cs}_2\text{AgBiBr}_6$, more efforts are required before new promising double perovskites for optoelectronic applications can be identified. Meanwhile, the benchmark double perovskites $\text{Cs}_2\text{AgBiBr}_6$ and $\text{Cs}_2\text{AgInCl}_6$ either have a large indirect bandgap or large direct bandgap with parity-forbidden transitions, which greatly limit their optoelectronic applications. Therefore, more efforts should be taken in the future to modify the band structure of benchmark double perovskites or/and to further explore other new promising double perovskite candidates for efficient photovoltaic applications.

Chapter 3 Bandgap Engineering of Halide Double Perovskites

As discussed in Chapter 2, the reported HDPs usually show relatively large band gaps and indirect bandgap nature or direct bandgap with parity-forbidden transitions and/or no PL emission, hindering their further application in optoelectronic field. Therefore, finding effective strategies to overcome these issues of HDPs is highly desirable.

In general, changing the halide is a simple yet efficient method to tune the bandgaps of perovskites because their VBM is mainly derived from the states of halogen orbitals. The I-based perovskites usually show the lowest bandgap compared to the corresponding Br-based and Cl-based compounds. Up to now, the only reported I-based double perovskite is $\text{Cs}_2\text{AgBiI}_6$ nanocrystals, which were synthesized by Gamelin and coworkers through the anion exchange method by treatment with trimethylsilyl iodide (TMSI) (**Figure 3.1a**).⁸⁷ The conversion progress was identified by optical characterization and XRD data, as shown in **Figure 3.1b-d**. However, these $\text{Cs}_2\text{AgBiI}_6$ nanocrystals are easily decomposed into $\text{Cs}_3\text{Bi}_2\text{I}_9$ nanocrystals after being exposed to air for several days. It is noted that there is still no report about $\text{Cs}_2\text{AgBiI}_6$ in the bulk form (crystals and films), instead, only the $\text{Cs}_3\text{Bi}_2\text{I}_9$ byproduct is formed. For Br-based HDPs, only several stable compounds have been synthesized so far, such as $\text{Cs}_2\text{AgBiBr}_6$,⁵³ $(\text{CH}_3\text{NH}_3)_2\text{AgBiBr}_6$,⁸⁸ and $\text{Cs}_2\text{AgTlBr}_6$.^{57,58} Up to now, most of the reported stable HDPs are Cl-based compounds with a large bandgap.

Figure 3.1 (a) Schematic diagram of synthesis of $\text{Cs}_2\text{AgBiI}_6$ Nanocrystals.⁸⁷ (b) Absorption spectra illustrating the conversion of $\text{Cs}_2\text{AgBiBr}_6$ nanocrystals to $\text{Cs}_2\text{AgBiI}_6$ nanocrystals by treatment with increasing amounts of TMSI (reaction progresses from blue to red).⁸⁷ (c) Photograph of dilute toluene solutions of (Left to Right) $\text{Cs}_2\text{AgBiBr}_6$, $\text{Cs}_2\text{AgBiBr}_{5.2}\text{I}_{0.8}$, $\text{Cs}_2\text{AgBiBr}_{1.6}\text{I}_{4.4}$, and $\text{Cs}_2\text{AgBiI}_6$ nanocrystals.⁸⁷ (d) Powder XRD pattern of 9.9 nm $\text{Cs}_2\text{AgBiI}_6$ nanocrystals, compared to a calculated pattern.⁸⁷

To understand the underlying reason for poor stability of most I-based or Br-based HDPs, two important parameters, Goldschmidt tolerance factor t and the octahedral factor u , are important to predict their crystallographic stability. Since the tolerance factor t of almost all HDPs combined with frequently used cations (Cs^+ , Ag^+ , Na^+ , Cu^+ , Sb^{3+} , Bi^{3+} , In^{3+} , Fe^{3+} , Tl^{3+}) and anions (Cl^- , Br^- , I^-) are within the range of requirement for stable perovskites ($0.81 < t < 1.11$), the octahedral factor μ provides more insights for the formation of a stable BX_6 octahedra, as shown in **Figure 3.2**. Obviously, a lot of I-based and Br-based octahedrons show a small octahedral factor μ outside the stable region ($\mu < 0.41$), which would explain the instability of the corresponding HDPs. There are some special cases for stable HDPs with a small value of μ . For example, stable $\text{Cs}_2\text{NaFeCl}_6$ and $\text{Cs}_2\text{AgFeCl}_6$ double perovskites with μ value of only 0.36 for $[\text{FeCl}_6]^{3-}$. Therefore, Goldschmidt tolerance factor t and the octahedral factor u should not be the whole story. Some compounds (for example $\text{Cs}_2\text{CuBiCl}_6$, $\text{Cs}_2\text{AgBiI}_6$ (bulk form)),

$\text{Cs}_2\text{NaBiI}_6$) with both appropriate Goldschmidt tolerance factor t and the octahedral factor μ cannot be synthesized experimentally. Along this line, Mitzi and co-workers found that Cu^{1+} -based halide compounds are more energetically favorable within 4-fold coordination, rather than 6-fold coordination for $[\text{CuX}_6]^{5-}$ octahedra, which rationalizes why $\text{Cs}_2\text{CuBiCl}_6$ cannot be formed. In addition, the thermodynamic stability of $\text{Cs}_2\text{AgBiI}_6$ was systematically studied using DFT by constructing its compositional phase diagram.⁸⁹ Results indicate that the $\text{Cs}_3\text{Bi}_2\text{I}_9$ byproduct is much stable than $\text{Cs}_2\text{AgBiI}_6$, which is consistent with the unsuccessful synthesis of $\text{Cs}_2\text{AgBiI}_6$ crystals or films. Similarly, $\text{Cs}_2\text{NaBiI}_6$ also tends to form the $\text{Cs}_3\text{Bi}_2\text{I}_9$ byproduct. In all, the small octahedral factor μ ($\mu < 0.41$), unfavorable B-site coordination number, and thermodynamic instability could be responsible for the instability of most I-based or Br-based HDPs.

Figure 3.2 The octahedral factor μ of various octahedrons.

Halide mixing is another feasible approach to increase the octahedral factor μ to form stable alloyed HDPs with a reduced bandgap. However, this well-established strategy for halide lead-based perovskites is not always efficient for narrowing the bandgap of HDPs. Take $\text{Cs}_2\text{AgBiX}_6$ ($\text{X} = \text{Cl}^-$, Br^- and I^-) as an example; the Cl^- can be alloyed into $\text{Cs}_2\text{AgBiBr}_6$ in any ratio with increasing the bandgap of the host material, while only a low level (< 3 mol % I^-) can be doped into the $\text{Cs}_2\text{AgBiBr}_6$ and $\text{Cs}_2\text{AgBiCl}_6$ host lattice. Further increasing I^- will lead to a phase segregation of silver-rich and bismuth-rich non-perovskite compounds (**Figure 3.3**).⁹⁰ Therefore, It is highly desirable to find other effective strategies to adjust the bandgap of HDPs.

Figure 3.3 Schematic representation of the $\text{Cs}_2\text{AgBiX}_6$ ($\text{X} = \text{Cl}/\text{Br}$, Br/I and Cl/I) miscibility.⁹⁰

3.1 Metal Doping/Alloying

Doping/alloying is a common method to tune the bandgap and/or change the direct/indirect nature of bandgap of semiconductors. For HDPs, two different B-site metal ions provide more degrees of freedom in selecting the suitable doping/alloying ions for HDPs. In general, it includes isovalent (monovalent and trivalent) and heterovalent (bivalent and tetravalent) metal doping/alloying.

3.1.1 Monovalent Metal Doping/Alloying

The first successful example was a dilute Tl^+ doped HDPs $\text{Cs}_2\text{AgBiBr}_6$ with a 0.1 eV bandgap reduction, developed by Karunadasa and coworkers in 2017. Interestingly, calculation results indicated that Tl^+ doping could convert the indirect bandgap to a direct bandgap. This was explained by hybridization of Tl p states with Br p and Bi p orbitals with decreasing the energy of the CBM at Γ and creating a direct bandgap (**Figure 3.4a**).⁹¹ It is noted that Tl is about ten times more toxic than Pb, which should be considered with respect to any practical application of Tl-doped double perovskites. Later, we developed a nontoxic and more efficient dopant Cu^+ , which can broaden the absorption profiles of $\text{Cs}_2\text{AgBiBr}_6$ from ~ 610 to ~ 860 nm (**Figure 3.4b**).⁹² We also found that the strong near-infrared range (NIR) absorption of Cu-doped $\text{Cs}_2\text{AgBiBr}_6$ is related to the sub-bandgap states (defect states) in the bandgap. More interestingly, these sub-bandgap states can generate considerable band carriers through NIR excitation (**Figure 3.4c**), implying a great potential application of Cu-doped $\text{Cs}_2\text{AgBiBr}_6$ in NIR photodetector. Recently, a series of Ag^+ doped/alloyed $\text{Cs}_2\text{NaFeCl}_6$ perovskite single crystals have been synthesized by partial/complete substitution of monovalent Na^+ with Ag^+ .⁹³ As shown in **Figure 3.4d**, the absorption edge of $\text{Cs}_2\text{NaFeCl}_6$ was significantly broadened from 600nm to the near-infrared range (800nm) after Ag-doping/alloying. Meanwhile, calculations show that the incorporation of Ag^+ could increase the electron mobility and carrier diffusion length.

Figure 3.4 (a) Band structures of $\text{Cs}_2(\text{Ag}_{1-a}\text{Bi}_{1-b})\text{Tl}_x\text{Br}_6$ ($x = 0.06$) for substitution of Tl^+ for Ag^+ . Metal orbital characters of the bands are shown in color.⁹¹ (b) Normalized UV-vis absorption of pristine $\text{Cs}_2\text{AgBiBr}_6$ (Cu-0) and Cu-doped $\text{Cs}_2\text{AgBiBr}_6$ (Cu-1, Cu-10, Cu-30, Cu-50) double perovskites. The inset shows the optical images of Cu-0 and Cu-doped Cu-50.⁹² (c) The photoconductance spectra of the $\text{Cs}_2\text{AgBiBr}_6$ (Cu-0) and $\text{Cs}_2(\text{Ag:Cu})\text{BiBr}_6$ (Cu-50) single crystals at room temperature.⁹² (d) UV-vis spectra of the $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{FeCl}_6$ ($x = 0, 0.06, 0.10, 0.58, 0.89, 1$) single crystals. The inset shows the optical images of $\text{Cs}_2\text{NaFeCl}_6$ and $\text{Cs}_2\text{AgFeCl}_6$.⁹³

In addition to bandgap narrowing, another possible merit of metal doping/alloying is to bring attractive emission properties. A typical example is Na^+ doped $\text{Cs}_2\text{AgInCl}_6$ with a direct bandgap. It is worth mentioning that pure $\text{Cs}_2\text{AgInCl}_6$ suffers from a low PLQY (<1%) due to the parity forbidden transition from the CBM to VBM. Fortunately, Tang and coworkers demonstrated that the monovalent Na^+ doping/alloying can break the parity forbidden transition in $\text{Cs}_2\text{AgInCl}_6$ by manipulating the symmetry of electron wavefunction at the Ag site (**Figure 3.5a**).⁶⁸ Meanwhile, incorporated $[\text{NaCl}_6]^{5-}$ octahedra serve as barriers to confine the spatial distribution of the STEs (**Figure 3.5b**), thus enhancing the electron and hole orbital overlap and increasing the transition dipole moment. As a result, the PL intensity of white emission was enhanced by three orders of magnitude after Na doping, as shown in **Figure 3.5c**.

Figure 3.5 (a) Parity change of the electron wavefunction (isosurface at the Ag site) of the STE before and after Na incorporation.⁶⁸ (b) Configuration showing the strengthened STE confinement by the surrounding $[\text{NaCl}_6]^{5-}$ octahedra. The STEs are confined within two lattice parameters surrounded by the $[\text{NaCl}_6]^{5-}$ octahedra. In (a) and (b), the cyan and magenta isosurfaces denote electrons and holes, respectively.⁶⁸ (c) Optical absorption (solid lines) and photoluminescence (dashed lines) spectra of pure $\text{Cs}_2\text{AgInCl}_6$ and $\text{Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6$.⁶⁸

3.1.2 Trivalent Metal Doping/Alloying

Compared with monovalent doping/alloying, trivalent metal doping/alloying is more widely used in HDPs since more than 34 elements can occupy the B^{3+} site in HDPs. An example is that partial substitution of Bi^{3+} with Tl^{3+} can reduce the bandgap of $\text{Cs}_2\text{AgBiBr}_6$ by 0.8 eV, while the band gap remained indirect (**Figure 3.6a**).⁹¹ Mitzi and coworkers employed nontoxic Sb^{3+} and In^{3+} to tune the bandgap of $\text{Cs}_2\text{AgBiBr}_6$.⁹⁴ As shown in **Figure 3.6 b,c**, up to 75% In^{3+} can be alloyed in the $\text{Cs}_2\text{AgBiBr}_6$ lattice with increased bandgap to 2.27 eV, and up to 37.5% Sb^{3+} can be alloyed in the lattice with decreased the bandgap to 1.86 eV. The different directions (decrease or increase) of bandgap changes were explained by the different band structures caused by different atomic configurations of Sb^{3+} and In^{3+} . Interestingly, Sb^{3+} was also employed to narrow the bandgap of $\text{Cs}_2\text{AgBiBr}_6$ thin films with an enhanced PCE compared with that of unalloyed $\text{Cs}_2\text{AgBiBr}_6$ solar cells.⁹⁵

Recently, transition metal Fe^{3+} is also attractive for doped/alloyed HDPs. For instance, our group doped magnetic element Fe^{3+} into optoelectronic double perovskite $\text{Cs}_2\text{AgBiBr}_6$ with the formation of halide perovskite alloys $\text{Cs}_2\text{Ag}(\text{Bi:Fe})\text{Br}_6$ (**Figure 3.6 d**).⁹⁶ Afterwards, we have successfully alloyed Fe^{3+} into the benchmark $\text{Cs}_2\text{AgInCl}_6$, tuning the bandgap of $\text{Cs}_2\text{AgIn}_{1-x}\text{Fe}_x\text{Cl}_6$ ($x = 0-1$) from 2.8 eV to 1.6 eV (**Figure 3.6 e,f**).⁶⁷ We further reveal the atomic-level structure of $\text{Cs}_2\text{AgIn}_{1-x}\text{Fe}_x\text{Cl}_6$ alloys using solid state NMR measurements. Our results indicate that Fe^{3+} substitutes In^{3+} in the lattice with the formation of $[\text{FeCl}_6]^{3-} \cdot [\text{AgCl}_6]^{5-}$ domains, which grow larger gradually as the

Fe^{3+} concentration increases. These domains could be further connected to form microscopically segregated Fe^{3+} -rich phases in the double perovskite alloys. The ferromagnetic or antiferromagnetic properties Fe^{3+} potentially bring the application of Fe^{3+} based HDPs for spintronics.

Figure 3.6 (a) Band structures of $\text{Cs}_2(\text{Ag}_{1-x}\text{Bi}_{1-x})\text{Tl}_x\text{Br}_6$ ($x = 0.06$) for substitution of TI^{3+} for Bi^{3+} .⁹¹ Metal orbital characters of the bands are shown in color. Indirect Tauc plots of (b) $\text{Cs}_2\text{AgBi}_{1-x}\text{In}_x\text{Br}_6$ and (c) $\text{Cs}_2\text{AgBi}_{1-x}\text{Sb}_x\text{Br}_6$.⁹⁴ (d) Photographs and crystal structures of double perovskites $\text{Cs}_2\text{AgBiBr}_6$ and Fe-doped $\text{Cs}_2\text{AgBiBr}_6$.⁹⁶ (e) Normalized UV-vis absorption spectra of $\text{Cs}_2\text{AgIn}_{1-x}\text{Fe}_x\text{Cl}_6$ ($x = 0.00, 0.01, 0.04, 0.32, 0.71$ and 1.00) crystals.⁶⁷ (f) Bandgaps of $\text{Cs}_2\text{AgIn}_{1-x}\text{Fe}_x\text{Cl}_6$ extracted by linear fits to both direct bandgap and indirect bandgap Tauc plots. Inset: Photographs of $\text{Cs}_2\text{AgInCl}_6$, $\text{Cs}_2\text{AgIn}_{0.99}\text{Fe}_{0.01}\text{Cl}_6$ and $\text{Cs}_2\text{AgFeCl}_6$ crystals.⁶⁷

Along with the bandgap changes, the direct and indirect nature of the band gap in HDPs could also be changed after trivalent metal doping. In 2017, McQueen and co-workers presented an alloying strategy for tuning the convergence of direct and indirect bandgaps based on chemical adjustment of the s- and p-orbital character of the CBM.⁵⁹ As shown in **Figure 3.7a**, with increasing percentage of Sb^{3+} in $\text{Cs}_2\text{AgSb}_x\text{In}_{1-x}\text{Cl}_6$ solid solutions, the contribution of $\text{Sb-}5s^2$ state to the valence bands increases and that of $\text{In-}5s^0$ state to the conduction bands decreases. Then, the direct to indirect band gap transition occurred at $x = 0.4$. Recently, a series of Bi^{3+} alloyed $\text{Cs}_2\text{Bi}_{1-x}\text{In}_x\text{AgCl}_6$ HDPs have been proposed, and these alloys span the indirect to direct bandgap modification (**Figure 3.7b**).⁹⁷ DFT calculations indicated that CBM is moved from the L symmetry point to near the Γ point after 75% In^{3+} alloying, composing a direct Γ - Γ band gap, as shown in

Figure 3.7c. Additionally, these alloys are capable of broadband white light PL emission upon ultraviolet excitation, and the maximum PLQY reached $34 \pm 4\%$ for $\text{Cs}_2\text{Bi}_{0.085}\text{In}_{0.915}\text{AgCl}_6$, which is promising for solid-state white-light emitting applications.

Figure 3.7 (a) The schematic representation of the proposed band diagram of $\text{Cs}_2\text{AgSb}_x\text{In}_{1-x}\text{Cl}_6$.⁵⁹ (b) Tauc plots showing indirect ($x \leq 0.5$, gray) and direct ($x > 0.50$, red) band gaps (b) for $\text{Cs}_2\text{Bi}_{1-x}\text{In}_x\text{AgCl}_6$ ($0 \leq x \leq 1$).⁹⁷ (c) Indirect to direct band gap transition of $\text{Cs}_2\text{Bi}_{1-x}\text{In}_x\text{AgCl}_6$ by using the calculated electronic band structure.⁹⁷

Rare-earth ions with trivalent can also be introduce into HDPs as an isovalent fashion. For example, lanthanide ions (Yb^{3+} and Er^{3+}) have been introduced to replace In^{3+} in $\text{Cs}_2\text{AgInCl}_6$ nanocrystals, and the characteristic f-f transition emission of Yb^{3+} at 996nm and Er^{3+} dopants at 1537nm have been observed.⁹⁸ Recently, Nag and co-workers further codoped Bi^{3+} in $\text{Yb}^{3+}/\text{Er}^{3+}$ doped $\text{Cs}_2\text{AgInCl}_6$ to significantly enhance the intensity of near-infrared emission.⁹⁹ This is possibly due to Bi-codoping can decrease the excitation energy that leads to the absorption of lower-energy photons. The excitation energy is then transferred to Er^{3+} and Yb^{3+} f electrons, which de-excite by emitting light at 1540 and 994 nm, respectively (**Figure 3.8a-c**). This codoping strategy may open a new chapter in the application of halide double perovskites in infrared detection and human sensing.

Figure 3.8 PL spectra of powder samples (Yb^{3+} -doped or Bi^{3+} - Yb^{3+} codoped $\text{Cs}_2\text{AgInCl}_6$ (a) and Er^{3+} -doped or Bi^{3+} - Er^{3+} codoped $\text{Cs}_2\text{AgInCl}_6$ (b)) mixed with BaSO_4 for quantitative comparisons of intensity.⁹⁹ Excitation at 370 nm. Inset figure in (b): NIR emission from Bi^{3+} - Er^{3+} codoped $\text{Cs}_2\text{AgInCl}_6$ coated on a commercial UV LED. (c) Comparing optical absorption and emission processes in Bi^{3+} - Er^{3+} codoped $\text{Cs}_2\text{AgInCl}_6$ with that of the undoped sample. Very weak or no emission is observed for undoped $\text{Cs}_2\text{AgInCl}_6$.⁹⁹

3.1.3 Heterovalent Metal Doping/Alloying

Apart from isovalent (mono--, trivalent--) doping, heterovalent doping (bivalent) has also been investigated to enhance the absorption and emission properties of HDPs. For example, Karunadasa and co-workers demonstrated that $\text{Sn}^{2+}/\text{Sn}^{4+}$ doping in $\text{Cs}_2\text{AgBiBr}_6$ resulted in a band gap reduction of up to 0.5 eV (**Figure 3.9a**).¹⁰⁰ The reduced bandgap relates to the introduction of Sn impurity bands below the CBM of the host material, as indicated by DFT calculations. Sn^{2+} replaces the position of Ag^+ while Sn^{4+} replaces the position of Bi^{3+} , collectively generating Ag^+ vacancies to maintain charge neutrality, as shown in **Figure 3.9b**. Another example is Cu^{2+} doped $\text{Cs}_2\text{AgSbCl}_6$ with reduced band gap from approximately 2.6 eV to approximately 1 eV (**Figure 3.9c**).¹⁰¹

Figure 3.9 (a) UV-vis absorbance spectra of crystals of $\text{Cs}_2\text{AgBiBr}_6$ and Sn-alloyed $\text{Cs}_2\text{AgBiBr}_6$ converted from diffuse reflectance spectra using the Kubelka–Munk transformation.¹⁰⁰ (b) The crystal structure of $\text{Cs}_2\text{AgBiBr}_6$ and an illustration of the substitution mechanism of Sn in crystals to yield Sn-alloyed $\text{Cs}_2\text{AgBiBr}_6$. Orange, gray, turquoise, and brown spheres represent Bi, Ag, Cs, and Br atoms, respectively.¹⁰⁰ (c) UV–vis diffuse reflectance (solid lines) and normalized absorption (dotted lines) spectra for $\text{Cs}_2\text{SbAgCl}_6$ parent ($x = 0.00$) and the maximum Cu^{2+} -doped ($x = 0.10$) materials.¹⁰¹

The Mn^{2+} doping/alloying strategy provide an efficient method to synthesize orange-red emitting phosphors based on the ${}^4\text{T}_1\text{-}{}^6\text{A}_1$ transition of octahedral Mn^{2+} , which is largely insensitive to structure of the host material. In 2018, Nag and co-workers first reported the Mn^{2+} doping/alloying in $\text{Cs}_2\text{AgInCl}_6$, which yields a red color emission (**Figure 3.10a**).⁸² Later, Mn^{2+} was also doped into $\text{Cs}_2\text{NaBiCl}_6$, leading a bright orange-red emission centered at 590nm.¹⁰² Meanwhile, a new family of Mn^{2+} -doped $\text{Cs}_2\text{NaBi}_{1-x}\text{In}_x\text{Cl}_6$ crystals have been synthesized with a strong orange-red emission in the range of 577 to 585nm.⁷⁰ As shown in **Figure 3.10b** all PLE spectra are corresponding to the transitions of Mn^{2+} from ground states of ${}^6\text{A}_1({}^6\text{S})$ to excited states of ${}^4\text{T}_1({}^4\text{P})$, ${}^4\text{T}_2({}^4\text{D})$, and ${}^4\text{T}_2({}^4\text{G})$, respectively. Meanwhile, the PL emission intensities gradually increased with the increase of In^{3+} concentration and reached the maximum in the $\text{Cs}_2\text{NaBi}_{0.8}\text{In}_{0.2}\text{Cl}_6$.

Figure 3.10 (a) PL spectra of Mn-doped $\text{Cs}_2\text{AgInCl}_6$ with different Mn contents, after excitation with 340 nm light. Insets show the photographs of luminescence from the powder samples under UV light.⁸² (b) PLE and PL spectra of $\text{Cs}_2\text{NaBi}_{1-x}\text{In}_x\text{Cl}_6:0.03\text{Mn}^{2+}$.⁷⁰

In conclusion, metal doping is a simple yet efficient strategy to modify the band structure of host HDPs, which can turn the bandgap values and/or change the indirect and direct bandgap nature. Meanwhile, the emission properties could also be changed after metal doping due to the breaking the parity-forbidden transition between bandgap or emission from dopant ions (such as Mn^{2+} , Yb^{3+} and Er^{3+}). Since both isovalent (monovalent and trivalent) and heterovalent (bivalent and Tetravalent) metal ions can be doped/alloyed into double perovskites, the considerable compositional diversity of double perovskites has been further expanded. This metal doping/alloying strategy provides more freedom and opportunity to search suitable compounds for high efficiency optoelectronic and/or multifunctional devices.

3.2 Crystallization Control

The optical and electronic properties of HDPs are highly correlated with the crystallization processes. The hydrothermal method is widely used to synthesize high-quality HDPs. In this approach, the crystallization process can be easily controlled by tuning the concentration of the precursor solution. For instance, the $\text{Cs}_2\text{AgInCl}_6$ single crystals grown from 0.076 M solution show higher transparency, lower trap density and higher carrier mobility than those grown from 0.05 M solution.⁶⁵ With increasing volumes of solvent (HCl) from 0.5 mL to 1.5 mL, the color of obtained $\text{Cs}_2\text{AgSbCl}_6$ powders can be continuously changed from yellow to near black (**Figure 3.11a**),¹⁰³ related to the different magnitude of reflectance for visible light (the dark sample absorbs more visible light) (**Figure 3.11b**) and the optical bandgap changing from 2.61 eV to 2.24 eV (**Figure 3.11c**). The underlying reason for the bandgap changes is possibly the formation of anti-site defect, established using DFT calculations. The calculated bandgap with Ag-Sb anti-site structures shows a decreased bandgap compared with that of Ag-Sb balanced structure, which is consistent with the bandgap narrowing in these powders, indicating that the darker samples possibly form more Ag-Sb defects (Ag-Sb disorder) during the crystallization process.

Figure 3.11 Powder XRD patterns (a), UV-vis diffuse reflectance spectra (b), and Tauc plots (c) of different as-prepared $\text{Cs}_2\text{AgSbCl}_6$ obtained by using different amounts of HCl (0.5, 0.75, 1.0, 1.25 and 1.5 mL) with variable visible light absorbance.¹⁰³

Besides the concentration, additive-assisted crystallization strategy was adopted to synthesize double perovskites with different bandgaps. For example, the absorption

band of $\text{Cs}_2\text{AgBiBr}_6$ single crystals from the phenylethylamine bromide (PEABr) additive precursor (PEA- $\text{Cs}_2\text{AgBiBr}_6$) exhibits a slight blueshift compared with the pristine $\text{Cs}_2\text{AgBiBr}_6$ (**Figure 3.12a**).¹⁰⁴ This blueshift can be explained by the enlarged bandgap of the PEA- $\text{Cs}_2\text{AgBiBr}_6$ crystals caused by the increased degree of Ag-Bi order, possibly due to that the selective coordination of the functionalized phenyl and ammonium ions in PEA^+ enables the formation of alternatively ordered arrangement of Ag^+ and Bi^{3+} ions, as shown in **Figure 3.12b**. Moreover, the PEA- $\text{Cs}_2\text{AgBiBr}_6$ crystals show reduced defect density and enhanced carrier mobility, which consequently promotes its application in an X-ray detector.

Figure 3.12 (a) UV-vis absorption spectra of pristine $\text{Cs}_2\text{AgBiBr}_6$ and PEA- $\text{Cs}_2\text{AgBiBr}_6$ single crystals with different PEABr concentration.¹⁰⁴ (b) Schematic view of the PEA-induced ordered arrangement of Ag^+ and Bi^{3+} ions in $\text{Cs}_2\text{AgBiBr}_6$ single crystals.¹⁰⁴

Slow evaporation of precursor solution is another well-known technique to grow perovskite single crystals. In this approach, we found that the evaporation temperature has a significant effect on the optical bandgaps of $\text{Cs}_2\text{AgBiBr}_6$ single crystals. As shown in **Figure 3.13a,b**, the $\text{Cs}_2\text{AgBiBr}_6$ single crystals synthesized from high evaporation temperature (150 °C, DP-150) exhibit darker color than those synthesized from low evaporation temperature (60 °C, DP-60), implying a wider absorption range.¹⁰⁵ The absorption broadening is further confirmed by UV-vis absorbance spectra, in which the absorption edge of DP-150 crystals shows an obvious red-shift of approximately 90 nm compared with the DP-60 crystal (**Figure 3.13c**). More importantly, the PL spectrum of DP-150 exhibits an obvious red shift compared with that of DP-60 (**Figure 3.13d**), which is consistent with the red shift in absorption spectra, indicating that the absorption edge shift results from the band gap narrowing effect. It is worth noting that the bandgap of DP-150 crystal calculated from the Tauc plots is approximately 1.72 eV, which is the lowest value among all the reports for $\text{Cs}_2\text{AgBiBr}_6$ at ambient conditions.

Figure 3.13 (a) Procedure for the crystal growth of DP-60 and DP-150.¹⁰⁵ (b) Optical images and the crystal structure of the DP-60 and DP-150 single crystals.¹⁰⁵ Normalized UV/Vis absorption spectra (c) and PL spectra (d) of DP-60 and DP-150 single crystals.¹⁰⁵

A possible explanation of the observed band gap narrowing is an increased level of Ag–Bi disorder in DP-150 as compared to DP-60. As shown in **Figure 3.14**, our functional theory (DFT) calculations indicate that a low-level disorder would introduce an acceptor-like defect state of Bi-p/Br-p character into the band gap. As the degree of disorder further increases, this defect state moves deeper into the gap and another, progressively broader set of defect states are formed below the conduction band edge.¹⁰⁵

Figure 3.14 Calculated total and partial electronic density of states for a set of $\text{Cs}_2\text{AgBiBr}_6$ structures with varying degrees of Ag–Bi disorder. The energy, E , is set to zero at the highest occupied state for each separate structure.¹⁰⁵

In all, the optical bandgap of HDPs can be modified by the crystallization control method, which can be affected by precursor concentration, additives, and different evaporation temperatures. The main reason is possibly related to different degrees of B-site disorder in the crystal under different crystallization processes. Additionally, several first-principle studies indicated that increasing B-site disorder has a large impact on the band structure and decreases the band gap.^{106,107} These investigations indicate that controlling the degree of B-site disorder by adjusting the crystallization process could be an effective way for band structure engineering of the HDPs for various applications.

3.3 Structure Engineering

The optical and electronic properties of HDPs are also related to the lattice structure, which can be tuned by physical treatment, such as high pressure or high temperature treatment. Among them, high pressure treatment usually introduces lattice contraction, while high temperature treatment always produces lattice expansion. Interestingly, the opposite structural behavior during the different physical treatment can cause similar bandgap changes with different mechanisms.

3.3.1 High-Pressure Treatment

High-pressure technology is a widespread and controllable method to continuously modify the lattice structure and electronic configuration of materials. In 2017, Zou and co-workers investigated the structure–bandgap relationship in HDP $\text{Cs}_2\text{AgBiBr}_6$ under

high pressure for the first time.¹⁰⁸ As shown in **Figure 3.15a**, in the low-pressure region (< 3 GPa), the bandgap of $\text{Cs}_2\text{AgBiBr}_6$ showed a slight narrowing, ascribed to the shrinkage of Bi-Br-Ag bonds and the homogenous octahedral contraction (which promote the overlap of elemental orbitals). With increasing pressure from 3.0 GPa to 4.0 GPa, the cubic phase of $\text{Cs}_2\text{AgBiBr}_6$ gradually transit into a tetragonal phase, confirmed by the angle-dispersive synchrotron X-ray diffraction (ADXRD) results (**Figure 3.15b**). In tetragonal $\text{Cs}_2\text{AgBiBr}_6$, the octahedral distortion and tilt result in less coupling between Bi 6p/ Ag 4d and Br 4p orbitals, corresponding to the bandgap widening between 4.0 GPa and 6.5 GPa. Impressively, the bandgap of $\text{Cs}_2\text{AgBiBr}_6$ decreased from 2.3 eV to 1.7 eV as the pressure further increased from 6.5 GPa to 15 GPa. This phenomenon could be explained by the subsequent structural amorphization of tetragonal $\text{Cs}_2\text{AgBiBr}_6$ at high pressure (**Figure 3.15b**). Equally important, the narrowed bandgap can be partially retained after releasing pressure, owing to the presence of residual amorphous phase in recovered $\text{Cs}_2\text{AgBiBr}_6$. Besides, the authors also applied high-pressure treatment to $\text{Cs}_2\text{AgBiBr}_6$ nanocrystals, which exhibited a similar phase transition from cubic to tetragonal compared to its bulk material, though at a relatively low pressure (2.3 GPa).¹⁰⁹ Meanwhile, its bandgap narrowed first and then widened as the pressure increased. It is noted that the bandgap of recovered $\text{Cs}_2\text{AgBiBr}_6$ nanocrystals was slightly wider compared with that of the initial one under ambient conditions, which could be associated with the significant size inhomogeneity of the decompressed samples.

Figure 3.15 (a) Band gap evolution of the $\text{Cs}_2\text{AgBiBr}_6$ crystal at high pressure, and the representative optical micrographs showing piezochromic transitions.¹⁰⁸ (b) Representative ADXRD patterns of $\text{Cs}_2\text{AgBiBr}_6$ perovskite at selected pressures.¹⁰⁸

The emission features of HDPs could also be affected by high-pressure treatment. For example, the PL emission of the $\text{Cs}_2\text{AgBiBr}_6$ thin films broadened significantly at a pressure above 4.6 GPa (**Figure 3.16a**).¹¹⁰ The phase transition from cubic to tetragonal and the increased octahedral tilting are responsible for this bandwidth broadening of PL emission. More importantly, such intriguing broad emission ranging from 520 to 1000 nm was retainable after the pressure was fully released due to the incomplete recrystallization. The pressure-dependent emission was also observed in $\text{Cs}_2\text{AgBiCl}_6$.¹¹¹ As shown in **Figure 3.16b**, $\text{Cs}_2\text{AgBiCl}_6$ exhibited an abnormal blue shift of the emission peak with high pressure because lattice compression in the cubic phase decreased lattice relaxation energy. The pressure-dependent emission spectra further indicated that lattice compression could effectively alter the electron–phonon coupling strength in HDPs, as the emission of $\text{Cs}_2\text{AgBiCl}_6$ is ascribed to electron–phonon coupling induced self-trapping excitons.

Figure 3.16 (a) Normalized PL spectra of $\text{Cs}_2\text{AgBiBr}_6$ films under pressure.¹¹⁰ (b) PL spectra of $\text{Cs}_2\text{AgBiCl}_6$ as a function of pressure during compression.¹¹¹

3.3.2 High-Temperature Treatment

Temperature is another well-known parameter that could cause lattice thermal expansion and modify carrier–phonon interactions, thus changing the optical properties of materials. Our group investigated the thermal-induced structural and optical change in HDP $\text{Cs}_2\text{AgBiBr}_6$ for the first time in 2019.⁶⁴ As shown in **Figure 3.17a**, the color of single crystals changed gradually from red to black with temperature increased from room temperature (RT) to 250 °C and returned to its original color after cooling. This reversible color transition is further confirmed by temperature-dependent UV–vis absorption spectra, where the absorption edge showed a red shift as the temperature increased and returned after cooling (**Figure 3.17b**). Since the color change process is fully reversible,

we also call this interesting phenomenon thermochromism. We further performed Ab Initio Molecular Dynamics (AIMD) simulations that can provide atomic-scale description of temperature-dependent material structural properties to reveal the mechanism underlying the thermochromism. **Figure 3.17c** shows the fluctuation of the bond lengths of Ag-Br and Bi-Br and the averaged bond length at 25 and 200 °C from the AIMD simulations. Based on the substantial fluctuations of the metal-halide bond lengths, we observed substantial broadening of the bands at both 27 °C and 227 °C, with the broadening more pronounced at 227 °C (**Figure 3.17d,e**). Such broadening of the bands at momentum points contributing to dipole-allowed transitions could have remarkable effect on optical properties. It is also noted that the spin-orbit coupling effect plays an essential role for the conduction band edge broadening. These results indicated that the anharmonic fluctuations of the Ag-Br and Bi-Br bonds and strong spin-orbit coupling are mainly responsible for thermochromism in $\text{Cs}_2\text{AgBiBr}_6$.⁶⁴

Figure 3.17 (a) Optical images of Single crystals at different temperatures for one heating-cooling cycle.⁶⁴ (b) UV-vis absorption spectra of single crystals at room temperature, 50 °C, 100 °C, 150 °C (RT-C, cooling to room temperature).⁶⁴ (c) Fluctuation of the bond lengths of Ag-Br and Bi-Br (top panel), and the averaged bond length (bottom panel) at 25 and 200 °C.⁶⁴ (d,e) Unfolded effective band structures including spin-orbit coupling (SOC) at 27 and 227 °C, respectively. The band structure at zero temperature is shown in black line. The color scale represents the weights of the unfolded bands, normalized to the interval [0, 1].⁶⁴

Besides, we further discovered another double perovskite $\text{Cs}_2\text{NaFeCl}_6$ with fully reversible thermochromism, showing a lower thermochromic operating temperature and wider color contrast compared with $\text{Cs}_2\text{AgBiBr}_6$. As shown in **Figure 3.18a**, the crystal color change gradually from light yellow to black in the range of 10–423 K. To quantify the color changes during temperature changes, we perform the UV-vis transmittance and diffuse reflectance measurements on $\text{Cs}_2\text{NaFeCl}_6$ crystal at different temperatures and convert them to pseudo absorbance spectra (**Figure 3.18b,c**). In the low temperature range of 6.8 K to 300 K, the absorption edge gradually shifts from $\sim 500\text{nm}$ to $\sim 570\text{nm}$ (**Figure 3.18b**). As the temperature further increases from RT ($\sim 300\text{ K}$) to 473 K, the absorption edge gradually redshifts to $\sim 670\text{nm}$ (**Figure 3.18c**), corresponding well with the observed crystal color changes. By extrapolating the linear region of the absorption edge to the energy-axis intercept, we determine the optical bandgaps of the $\text{Cs}_2\text{NaFeCl}_6$ crystals at different temperatures. At low temperatures ($\sim 6.8\text{ K}$ to 80 K) we find the characteristic weakly temperature dependent behaviour of the optical bandgap, which is followed by a rather steep decrease with temperature (**Figure 3.18d**). We find a discrepancy between the optical bandgap at 300K calculated from transmittance and reflectance results, which could be related to the unfavorable background in the reflectance spectra that has not been successfully removed experimentally. Our measurements of the optical bandgap compares very well to first-principles calculations of the temperature dependence of the electronic bandgap as shown in **Figure 3.18d**. Which indicates that the thermochromism of $\text{Cs}_2\text{NaFeCl}_6$ can be described as purely an effect of strong electron-phonon coupling.

Moreover, temperature-dependent crystal structure results show that only the Na-Cl bond length changes significantly during the heating/cooling process, while the Fe-Cl bond length changes are negligible. This behaviour is reproduced in our DFT calculations (**Figure 3.19a**). Interestingly, focusing on this bond-behaviour yields insight into the nature of the strong-electron phonon coupling in this system. In **Figure 3.19b** we plot the bandgap of $\text{Cs}_2\text{NaFeCl}_6$ as a function of volume for two separate cases. In the first, full atomic relaxation is performed at each volume, while in the second, the fractional coordinates are kept fixed at their relaxed value at the RT volume. We see that in the first case, the bandgap remains virtually constant, while in the second case, there is a clear change. On the one hand, this shows that thermal expansion has a very weak explicit effect on the temperature induced bandgap change. On the other hand, it indicates that the bandgap depends on the length of the Fe-Cl bond, and accordingly, to vibrations of the Cl atoms parallel to this bond.

Figure 3.18 (a) Optical images of $\text{Cs}_2\text{NaFeCl}_6$ single crystal at different temperatures. UV-vis absorption spectra of $\text{Cs}_2\text{NaFeCl}_6$ single crystal at low temperature range (b) and high temperature range (c) (RT: room temperature). (d) Plots of the optical bandgap of $\text{Cs}_2\text{NaFeCl}_6$ as a function of temperatures. The calculated bandgaps have been shifted to match the experimental values at the lowest temperature.

We confirm this by examining the dependence on the bandgap on the optical A_{1g} phonon mode at the Γ -point. The eigenvectors of this mode corresponds precisely to the motion of the Cl ion along the Na-Cl-Fe bonds, with positive/negative displacement amplitudes corresponding to elongation and shortening of the Fe-Cl bond, respectively. We find that the bandgap depends strongly, and in a highly unusual, non-parabolic, way, on this phonon mode, as shown in **Figure 3.19c**. Indeed, for positive amplitudes (bond elongation) the bandgap decreases rapidly. Upon close examination this decrease of the bandgap is found to be due to a shift down of the conduction band minimum (CBM). The electronic DOS (in the DLM magnetic state, see computational details) of $\text{Cs}_2\text{NaFeCl}_6$ is shown in **Figure 3.19d**, where we can see that the states that make up the CBM are highly localized Fe- t_{2g} states, while the main valence band is primarily of Cl-p character. Thus, the strong electron phonon coupling in $\text{Cs}_2\text{NaFeCl}_6$ can, at least to some degree, be understood in terms of a sensitive dependence of the localized Fe-d states on vibrations that alter the length of the Fe-Cl bond. Our results provide a new understanding on thermochromism in HDPs.

Figure 3.19 (a) Fe-Cl and Na-Cl bond lengths extracted from AIMD simulations. (b) Bandgap as a function of volume, for fully relaxed atomic positions (red circles) and for atomic positions fixed at the relaxed ones at the volume corresponding to RT. (c) Bandgap as a function of normal mode coordinates of the A_{1g} Γ -point phonon mode. The displacement of this mode corresponds to motion of the Cl atoms along the Na-Cl-Fe bonds. (d) Electronic DOS in the DLM state. All calculations with PBEsol+U (3eV).

In conclusion, through high-pressure or high-temperature physical treatment, the optical and/or electronic properties of HDPs can be altered without changing chemical composition. These changes during high-pressure treatment are associated with the octahedral contraction and distortion, phase transition and structural amorphization. However, for high temperature treatment, these changes are mainly related to the anharmonic fluctuations of the metal-halide bonds, spin-orbit coupling and electron-phonon coupling. These findings not only offer new strategies for the modulation and tuning of optical and electric properties of HDPs, but also provide novel insights into the structure-property relationship in HDPs.

Chapter 4 Crystal Synthesis and Characterization

Methods

4.1 Crystal Synthesis Methods

To understand the intrinsic properties of HDPs materials, it is crucial to synthesize high-quality single crystals, which are also important for single crystal device applications. In this chapter, various common techniques to grow the single crystal of halide perovskites are introduced, including the hydrothermal method,⁶⁷ slow evaporation method,¹¹² inversion temperature crystallization method¹¹³ and antisolvent vapor assisted method.¹¹⁴

4.1.1 Hydrothermal (Solvothermal) Method

Hydrothermal method is the most used technique to synthesize high-quality HDPs single crystals. In this method, the crystal growth is performed in a piece of equipment consisting of a steel pressure vessel called an autoclave, which can withstand high temperatures and pressures, as shown in **Figure 4.1 a,b**. Usually, the precursor materials have very poor solubility in the solvent at room temperature but can be fully dissolved under high temperature and high-pressure conditions. By decreasing the temperature of the precursor solution in the autoclave, the solubility of the solution gradually decreases and reaches supersaturation. Further decreasing the temperature of the precursor solution slowly, crystal nucleus forms and then grow into large crystals. For the growth of HDPs single crystals, a solvent (acid) is used instead of water in the synthesis process. We employed this method to synthesize most of HDPs crystals involved in this thesis, including $\text{Cs}_2\text{AgBiBr}_6$, Cu-doped $\text{Cs}_2\text{AgBiBr}_6$, $\text{Cs}_2\text{AgIn}_{(1-x)}\text{Fe}_x\text{Cl}_6$ and $\text{Cs}_2\text{NaFeCl}_6$ single crystals.

Figure 4.1 (a) Schematic diagram of Teflon lined stainless steel autoclave with inner components. The Teflon chamber is housed inside the stainless-steel chamber in which reaction is carried out. (b) The commercially available Teflon lined stainless steel autoclave.

4.1.2 Slow Evaporation Method

Slow evaporation method is the simplest technique for growing single crystals of air-stable materials. In this method, we need to choose a suitable solvent to prepare a nearly saturated precursor solution, and then slowly evaporate the solution to obtain single crystals, as shown in **Figure 4.2a**. The size of the perforations on the cap and the evaporation temperature are two experimental variables that depend to some extent on the volatility of the solvent. In this thesis, we employed this method to grow $\text{Cs}_2\text{AgBiBr}_6$ single crystals with different bandgaps by controlling the evaporation temperature (**Figure 4.2b**). The basic principle of crystal growth by slow evaporation method at different temperatures is almost the same, which is caused by the precipitation of solutes due to gradual evaporation of the solvent.

Figure 4.2 Schematic representation of crystal growth by slow evaporation method at room temperature (a)¹¹⁵ and high temperature (b).

4.1.3 Inversion Temperature Crystallization Method

Inversion temperature crystallization method is a general and simple method for synthesizing Pb-based halide perovskite single crystals. This method requires the material to have inverse solubility in an appropriate solvent at high temperatures. As shown in **Figure 4.3**, the single crystals can be precipitated by annealing the precursor solution at a high temperature due to the decreased solubility of material at high temperatures. For example, MAPbI_3 ($\text{MA} = \text{CH}_3\text{NH}_3^+$) single crystals can be obtained by dissolving a stoichiometric molar ratio of salts PbI_2 and MAI in γ -butyrolactone (GBL) solution at room temperature, followed by heating the precursor solution at 120 °C for several hours.

Since most HDPs have solubility issues or lack of suitable solvent for HDPs with inverse solubility at high temperature, this method has not been adopted to grow HDPs single crystals.

Figure 4.3 Schematic representation of the inversion temperature crystallization method in which the crystallization vial is immersed within a heating bath.¹¹⁵

4.1.4 Antisolvent Vapor Assisted Method

The critical part in this method is to choose two suitable solvents (solvent 1 and solvent 2). Solvent 1 is not or less volatile with a good solubility for the precursor materials. In contrast, solvent 2 is more volatile with extremely poor solubility of the precursor materials. For crystal growth, the precursor materials are dissolved in solvent 1 in a small vial, and then transferred to a sealed space with the solvent 2, as shown in **Figure 4.4**. Along with the slow diffusion of the solvent 2 into the precursor solution, single crystals would be formed.

Figure 4.4 Schematic illustration of antisolvent method for single crystal growth.¹¹⁵

4.2 Characterization Methods

4.2.1 X-ray Diffractometry (XRD)

X-ray diffraction (XRD) is the most used non-destructive technique to determine the crystallographic structure of a material. It works by irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that are scattered by the material. Specifically, crystals are regular arrays of atoms, and X-rays can be considered waves of electromagnetic radiation. Crystal atoms can scatter incident X-rays mainly through interaction with the atoms' electrons, called elastic scattering. A regular array of scatterers (atoms) produces a regular array of spherical waves and then

wave interference occurs. There are two different interference, constructive and destructive interference, of which only constructive interference can be detected in the X-ray detector. The constructive interference (diffraction) could occur in a special condition, as determined by Bragg's law:

$$n\lambda = 2d \sin \theta \quad (4-1)$$

here n is an integer, λ is the wavelength of the incident X-ray, d is the spacing between diffracting planes and θ is the incident angle (**Figure 4.5**).

Figure 4.5 Bragg's law

XRD can be performed using single crystal (single-crystal XRD) or powder (powder XRD). Single-crystal XRD is mainly used to determine the absolute structure of a single crystal, including the exact atomic positions, unit cell dimensions, bond lengths, and bond-angles. Powder XRD measures samples of polycrystalline materials (polycrystals) and is therefore considered a bulk characterization technique. The powder XRD pattern is considered a "fingerprint" for a given material; it provides information about the bulk purity, crystallinity, and phase (polymorph) of the material.

4.2.2 Ultraviolet and Visible Spectrophotometry (UV-Vis)

Ultraviolet–visible spectrophotometry (UV–Vis) primarily refers to absorption spectroscopy or reflectance spectroscopy in the near-UV (180–390 nm) or visible (390–780 nm) region. It measures the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. The absorbance of materials can be determined by using the Beer–Lambert law.

$$A = \log_{10}(I_0/I) \quad (4-2)$$

where A is the measured absorbance, I_0 is the intensity of the incident light at a given wavelength, I is the intensity of light after passing through a sample. Since the ratio I/I_0 is transmittance T , the absorbance A could be converted by transmittance using the below equation.

$$A = \log_{10} (1/T) = -\log_{10} T \quad (4-3)$$

It is noted that some powder or single crystal samples with the thick thickness could cause absorption saturation, that is, almost 100% of the light is absorbed. In this case, we could choose to measure the reflectance R instead of the absorbance A .

$$R = I'/I'_0 \quad (4-4)$$

Here I' is the intensity of light reflected from a sample, and I'_0 is the intensity of light reflected from a reference material, such as spectralon or BaSO₄. The reflectance spectra can be further converted to pseudo-absorbance spectra using the Kubelka-Munk transform.

$$\alpha \approx (1-R)^2/2R \quad (4-5)$$

where α is pseudo-absorbance and R is reflectance. In addition, the direct and indirect optical bandgaps can be measured by taking the intercept upon extrapolation of the linear regions of $(\alpha h\nu)^2$ Vs $E(\text{eV})$ and $(\alpha h\nu)^{1/2}$ Vs $E(\text{eV})$ plots, respectively.

4.2.3 Photoluminescence spectroscopy

Photoluminescence (PL) is luminescence from materials after the absorption of photons. In semiconductors, PL is a basic and important property, which is a radiative recombination process of electron-hole pairs. Generally, PL in perovskite semiconductors mainly includes band-to-band luminescence and exciton luminescence. As shown in **Figure 4.6**, band-to-band luminescence is the radiative recombination between the electrons in the conduction band and holes in the valance band. Therefore, this type of luminescence can be employed to determine the bandgap of materials. Exciton luminescence means the emission of photons through exciton recombination. Exciton is a bound electron-hole pair, in which an electron and a hole are attracted to each other by Coulomb force. The exciton emission energy is usually slightly lower than the bandgap, and this energy difference is the exciton binding energy. It is noted that there is a special type of exciton luminescence, called self-trapped exciton (STE) luminescence, whose emission energy is much smaller than the bandgap (**Figure 4.6**).

Figure 4.6 Schematic of various intrinsic photoluminescence phenomena, including band-to-band luminescence, exciton luminescence, and STE luminescence.⁶⁹

4.2.4 Solid-State Nuclear Magnetic Resonance (ssNMR)

Solid-state nuclear magnetic resonance (ssNMR) spectroscopy is an atomic-level method to determine the chemical structure of solid materials, and it is a type of nuclear magnetic resonance (NMR) spectroscopy. NMR is the response of nuclei with non-zero spins in a magnetic field to resonant excitation by radiofrequency irradiation (**Figure 4.7a**).¹¹⁶ When atoms with nuclei spins are placed in an external magnetic field B_0 , the degeneracy of the nuclear spin states is lifted (**Figure 4.7b**), leading to an energy difference ΔE given by below.

$$\Delta E = \gamma h(1 - \sigma)B_0 \quad (4-6)$$

where γ is the gyromagnetic ratio, a fundamental property associated with each isotope; h is Planck constant; B_0 is the strength of the external magnetic field; and σ is the chemical shielding around a nucleus, which varies for different nuclei of a given isotope in a material. The transitions between these nuclear spin states induced by electromagnetic radiation are called resonance. The resonance frequencies are sensitive to the electron distribution around the nucleus, which shields the nucleus from the external magnetic field. Meanwhile, the electron distribution of the nucleus could be affected by a series of couplings, including spin–spin scalar couplings dependent on covalent bonding, spin–spin dipolar couplings dependent on internuclear distances, and quadrupolar couplings between the electric field gradient at the nucleus and the charge distribution of the nucleus for nuclear spins greater than 1/2. Therefore, NMR frequencies can reveal the chemical environments of nucleus in material. For example, if nuclei are present in a compound in equivalent chemical environments, they will appear as one peak in the

spectra. Multiple peaks will be observed when the nuclei exist in more than one chemical environment. Since the changes in NMR frequency are usually extremely small, NMR frequencies are commonly transferred to chemical shift δ , which is the fractional difference between the frequency of a particular nucleus and a reference or standard compound such as tetramethylsilane. The unit of chemical shift δ is part per million (ppm).

Figure 4.7 (a)(b) Nuclear spin magnetic dipole moments (μ) precess around a static magnetic field (B_0) at a frequency identical to the transition frequency between the energy levels of the spins ($\Delta E = \hbar\omega_0$). A radiofrequency (RF) coil is wrapped around the sample at the top of a nuclear magnetic resonance (NMR) probe, which is inserted into the center of the magnet. The RF coil allows irradiation of the RF pulses as well as detection of the transition frequency of the nuclear magnetic moment.¹¹⁶ (b) Schematic diagram of nuclear spin energy level splitting under an external static magnetic field. Angular velocity, $\omega = -\gamma B$.¹¹⁶

The frequency-domain ssNMR spectra are obtained from Fourier transformation of time-domain signals recorded after a radiofrequency pulse that perturbs the system from equilibrium. The return to equilibrium after excitation by the pulse is referred to as longitudinal relaxation. The relaxation time of nuclei in diamagnetic perovskite materials

could be significantly shortened (up to 3–4 orders of magnitude) when paramagnetic ions such as some transition metal and lanthanide ions are introduced. This phenomenon called paramagnetic relaxation enhancements (PRE), arising from the electron spin-nuclear spin interactions between NMR active nuclei and unpaired electrons of the paramagnetic ion.¹¹⁷ PRE is a short-range effect and typically can be observed for distances up to around 20 Å from the unpaired electron. Therefore, the relaxation-based data provide a straightforward and general approach to evidence and understand the distribution of paramagnetic alloying ions in host materials.

In addition, ssNMR spectra usually show broad peaks (**Figure 4.8b**), which are caused by the significant effects of anisotropic (orientation dependent) nuclear spin interactions. Unlike the more commonly used solution NMR, the anisotropic interactions are averaged due to the rapid tumbling of the molecules in solution, but molecules in solids cannot tumble a lot and the orientation matters. To obtain solid-state NMR spectra with higher resolution (narrow peaks), a commonly used approach is magic-angle spinning (MAS), where samples are physically spun around an axis that is tilted by 54.7° from the static magnetic field to remove the anisotropic contribution (**Figure 4.8a**).¹¹⁸ The rate of MSA needs to be greater than (or equal to) the magnitude of the anisotropic interaction to average it to zero. Otherwise, a manifold of spinning sidebands becomes visible, which appear on either side of any large genuine peak at a separation of integer multiples to the spinning rate (**Figure 4.8c,d**).

Figure 4.8 (a) Schematic representation of MAS NMR setup.¹¹⁸ The sample is placed into an NMR probe at the "magic" angle of 54.74° with respect to the static magnetic field and spun rapidly. (b-d) Illustration of the effect of MAS on NMR line shapes in a spin- $1/2$ nucleus. The broad ^{13}C powder pattern resulting from chemical shift interaction in a static sample (b) is broken up into a series of spinning sidebands (c), which represent the Fourier components of the MAS frequency, and averaged out into an isotropic peak (d) when the MAS frequency exceeds the magnitude of the anisotropic interaction.¹¹⁸

Chapter 5 Summary and Outlook

In this thesis, we aim to solve the large and/or indirect bandgap issues of HDPs by employing three strategies, including metal doping/alloying, crystallization control and structure engineering. We also discuss the intrinsic characteristics, optoelectronic applications, critical challenges, and opportunities of HDPs.

Metal doping/alloying can change the bandgap of the host HDPs by the introduction of the external dopant's orbital states in the host band structure with a modification of the CBM and VBM. A special example we discovered is Cu-doped $\text{Cs}_2\text{AgBiBr}_6$. We found that Cu dopants barely affect the bandgap of the host; instead, it contributes to the noticeable near infrared (NIR) absorption by introducing defect states. More interestingly, this NIR absorption can generate band carriers upon excitation and thus demonstrate a novel approach for NIR detection in HDPs. In addition, the emission properties of host HDPs can also be changed, not only due to the bandgap modulation, but also caused by the dopant ions which emit light via their orbital transition emission, such as Mn^{2+} , Er^{3+} and Yb^{3+} . Moreover, a series of isovalent (monovalent and trivalent) and heterovalent (bivalent and tetravalent) metal ions can be doped or co-doped into HDPs lattice, further expanding the large family of HDPs. These results provide the possibility to fabricate various optoelectronic and multifunctional devices based on HDPs through doping/alloying different functional ions. However, due to the poor solubility of HDPs and the different crystallization process of thin films compared with single crystals, the formation of thin films of these materials is still challenging and requires further research.

The large bandgaps of HDPs can also be narrowed by crystallization control, which is possibly related to different degrees of B-site ($\text{B}^{\text{I}}/\text{B}^{\text{III}}$) disorder in the crystal under different crystallization processes. This has been verified by first-principles calculations, which clearly indicated that increasing B-site disorder has a huge impact on the band structure and could significantly reduce the bandgap. Unfortunately, there is still a lack of a promising approach to precisely control and detect the degrees of $\text{B}^{\text{I}}/\text{B}^{\text{III}}$ disorder in HDPs. Meanwhile, the formed anti-site defects by $\text{B}^{\text{I}}/\text{B}^{\text{III}}$ disorder are unfavorable for optoelectronic applications. Therefore, it is critical to find a balance between the decrease of bandgap and increase of anti-site defects in order to further utilize this order-to-disorder approach. Besides, the $\text{B}^{\text{I}}/\text{B}^{\text{III}}$ disorder in HDPs crystals or powders cannot be retained in thin films due to their different crystallization processes.

Structure engineering is another strategy to alter the band structure of HDPs by tuning the lattice structure through high-pressure or high-temperature physical treatment.

The underlying mechanisms of these two treatments are different. Specifically, during high-pressure treatment, the octahedral contraction and distortion, phase transition and structural amorphization are responsible for the bandgap change in HDPs. The bandgap change during high-temperature treatment is associated with the anharmonic fluctuations of the metal-halide bonds, spin-orbit coupling and electron-phonon coupling. A drawback of these strategies is that the engineered bandgap is hardly to be reserved at ambient conditions. However, these reversible process (i.e. thermochromism) could open doors for new applications of HDPs, such as smart windows or visual thermometers. Moreover, such widespread and controllable physical treatments provide a powerful tool for understanding the basic structure–property relationship of HDPs without changing the chemical composition.

In addition to the issues of large and/or indirect bandgap, some other challenges in HDPs also require attention. For example, the poor solubility make it challenge to fabricate most Cl-based HDPs films using the solution method, which impedes their application in thin film devices. Thermal evaporation could be an alternative to prepare high-quality thin films of HDPs with poor solubility. Additionally, no HDPs have emerged as a prospective solar absorber with promising photovoltaic properties similar to Pb-based halide perovskites. Further efforts are required to explore new promising HDPs with suitable direct bandgaps for efficient photovoltaic applications. Fortunately, some HDPs have shown exciting optoelectronic properties in luminescence and photodetection, indicating promising applications of currently reported HDPs as photo/X-ray detectors or phosphors in down-conversion light-emitting-diodes.

In summary, environmentally friendly HDPs have become a promising alternative to Pb halide perovskites for optoelectronic applications, in terms of their excellent stability, a wide range of possible combinations, and rich substitutional chemistry. However, the research on HDPs is still at an early stage, and more efforts are desired to realize their full potential by understanding and modifying their fundamental properties, as well as exploring other new promising HDPs and new applications.

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