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Structural and optical properties of highly emitting lead-free double perovskites
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Abstract

This thesis introduces lead-free double perovskite compounds with broad-band white light emission and the potential application of various doped and alloyed double perovskites in the illumination field. In addition, the mechanism of highly efficient warm white light emission is also studied.

Double perovskites are promising lead-free perovskite materials which alternatively replace the divalent Pb cations in lead-halide perovskite with a combination of a monovalent and trivalent cation. They exhibit excellent stability under moisture, heat and light. In this work, halide double perovskite materials such as Cs$_2$AgInCl$_6$, Cs$_2$NaInCl$_6$, Cs$_2$AgBiCl$_6$, and Cs$_2$NaBiCl$_6$ are firstly successfully synthesized and their potential application in the optoelectronic field is studied. Cs$_2$AgBiCl$_6$ and Cs$_2$NaBiCl$_6$ possess indirect band gaps while Cs$_2$AgInCl$_6$ and Cs$_2$NaInCl$_6$ have direct band gaps but the dipole transitions between the band edge states are parity-forbidden, which leads to relatively large optical band gaps. However, alloyed double perovskite materials Cs$_2$Na$_{1-x}$Ag$_x$In$_{1-y}$Bi$_y$Cl$_6$ show excellent properties for its highly efficient warm white emission which could be used as a single-component white light emitter. Here, transient absorption and photoluminescence are measured for investigating the outstanding emission properties of Cs$_2$Na$_{1-x}$Ag$_x$In$_{1-y}$Bi$_y$Cl$_6$.

Furthermore, Sb alloyed Cs$_2$NaInCl$_6$, Cs$_2$InCl$_5$.H$_2$O and Cs$_3$InCl$_6$ are also prepared which exhibit efficient blue, yellow and blue-green emission respectively under UV light. These materials are promising phosphor in lighting applications. The understanding of luminescence mechanism in double perovskite will help the search and the design of more efficient phosphors.
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CHAPTER 1  Introduction on phosphor and white emission mechanism

Because of their superior energy conversion efficiency, low cost, long lifespans and low operating temperature, solid state lighting (SSL) devices have obvious advantages to replace conventional incandescent and fluorescent lamps. It brings about a revolution in the lighting and display industries and is widely considered to be the lighting technology of the future. To generate white-light emission, typical SSL devices consist of light emitting diodes (LEDs) coated with phosphor by three methods: (i) mixing emitters with a mixture of phosphors, e.g., an ultraviolet (UV) LED coated with blue, green, and red phosphors, (ii) mixing emitters with two complementary lights in proper intensity ratios, e.g., a GaN-based blue LED chip coated with a YAG:Ce yellow-emitting phosphor, and (iii) a single-component broadband white light emitting phosphor pumped by a UV-LED. However, it is usually a complicated process to blend different emitters to realize desired white emissions. The mixing phosphors often result in efficiency losses due to self-absorption which cause bad reproducibility. For the blue-LED + YAG:Ce yellow phosphor, it emits white light with problem of poor color rendering index and low stability of color temperature. To simplify the fabrication process and overcome these problems, the single-component white light emitting materials is a highly promising solution. Recently, series halide perovskites with various structural dimensionality (0D, 1D, 2D, and 3D) have been reported in broadband white light emission which showed promising for SSL. Wherein, double perovskites exhibit extraordinary optoelectronic properties while avoiding unpleasant Pb toxicity issue and instability problem exist in lead halide perovskites. Double perovskites substitute the two divalent cations Pb2+ in single perovskite by a combination of a monovalent and trivalent cation, forming structure as ABX3 which maintain the 3D perovskite structure. Double perovskites are suggested as promising lead free perovskite materials and they have shown a remarkable stability in ambient atmosphere. In this thesis, it is interested to prepare single-component white light emitting materials from double perovskite, illuminate the underlying emission mechanism and explore their merit to find more extensive applications. Further introduction for double perovskites will be provided in next chapter. In this chapter, I will introduce some basic concepts and some models in the first two part and mechanisms of white light emission in the third part that are all important for the understanding of the subsequent chapters.
1.1 \textbf{Luminescence principle of phosphor}

The luminescent material, also known as phosphor, after irradiated by excitation sources such as cathode rays, X-rays, ultraviolet rays, etc., process of energy absorption and conversion occurs inside the material and finally emits light. Inorganic luminescent material consists of a host lattice and a luminescent center, often called an activator which is a foreign ion (dopant) and can be excited to luminescence (Figure 1.1a). The luminescence process in such a system are as follows, the exciting radiation is absorbed by the activator, raising it to an excited state. The excited state returns to the ground state by emission of radiation. However, in many luminescent materials the situation is more complicated when the exciting radiation is not absorbed by the activator. Then we can add another foreign ion to the host lattice which may absorb the exciting radiation and subsequently transfer it to a neighboring activator and thus inducing luminescence. Here, the absorbing is called sensitizer (Figure 1.1b) It should be emphasized that the activator has an absorption bandwidth that overlaps the emission bandwidth of sensitizer and no photons are emitted in such a process. Also, since nonradiative energy transfer is another deactivation channel, this process is accompanied by a decrease in the lifetime of the excited state of the sensitizer. Furthermore, energy transfer sometimes occurs between similar ions, resulting in concentration-dependent fluorescence and self-quenching\textsuperscript{14}.

![Figure 1.1](image)

\textit{Figure 1.1 Schematic energy level scheme (bottom) and diagrammatic representation of the role in the luminescence process (top) of an activator (A) doped in a host (H) lattice (a), and a sensitizer (S) and its relationship to an activator (A) and the host lattice (H) (b)\textsuperscript{15}.}
1.1.1 Luminescent center-host interactions

Let us consider an activator ion A placed at a site in host lattice, surrounded by an array of six regular lattice ions L (ligand ions), with a distance of “R” from the ion A. The ligand ions L are located at the corners of an octahedron, as shown in Figure 1.2. The set comprised of ion A and the six ligand ions L constitutes a pseudo-molecule, AL₆, which produces the appearance of new optical bands (not present in the undoped crystal) and is called an optically active center.

![Figure 1.2: A scheme of an illustrative optical center AL₆ complex inserted into the host lattice. This particular center consists of a dopant optical ion A in an octahedral environment of L ions.](image)

If we assume the ideal situation of a rigid (nonvibrating) lattice, the A–L distance “R” remains fixed and corresponds to the time-average positions in the vibrating case. In order to account for the optical absorption and emission bands of the AL₆ center, we must first determine its energy levels Eᵢ by solving the Schrödinger equation:

\[ H\psi_i = E_i\psi_i \] (1.1)

where H represents a Hamiltonian that includes the different interactions of the valence electrons in the AL₆ center and \( \psi_i \) are eigenfunctions of the center. Two main methodologies are commonly used to solve this equation: crystalline field theory (CFT) and molecular orbital theory (MOT)¹⁶.

1.1.1.1 Crystalline field theory

Crystal field theory assumes that the bonding between the central metal ion A and the ligands is completely ignored. The ligands are viewed simply as point charges. This thesis focuses on the valence d orbitals of the central transition metal ion and examines how the relative energies of the d orbitals change under the effect of negative point charges (the ligands). In the case of free ion, the energy values of the five degenerate d orbitals \( d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, \) and
$d_z^2$ are the same. If the distribution of the point charges is spherical then all $d$ orbitals will be affected in the same manner. All of the $d$ orbitals will rise in energy. However, in an octahedral arrangement, the point charges approach the metal atom along the Cartesian $x$, $y$ and $z$ axes which induces repulsive force in the system (Figure 1.3). The orbitals that lie along these axes ($d_{x^2-y^2}$, and $d_z^2$) should rise in energy by a greater amount compared to the orbitals that do not lie exactly along the $x$, $y$ and $z$ axes ($d_{xy}$, $d_{yz}$, $d_{xz}$).

![Figure 1.3 d orbitals and ligand interaction (octahedral field)](image)

Hence, the five degenerate $d$ orbitals undergo orbital splitting on the basis of the energy value of each $d$ orbital in the geometric structure. As shown in Figure 1.4, the five degenerate $d$ orbitals $d_{xy}$, $d_{yz}$, $d_{xz}$, $d_{x^2-y^2}$, and $d_z^2$ are split into $d_{x^2-y^2}$ and $d_z^2$ as doublet state ($E_g$) with high energy level and $d_{xy}$, $d_{yz}$ and $d_{xz}$ as triplet state ($T_{2g}$) with low energy structure, which is represented as $E_g$ and $T_{2g}$. The energy value difference between $E_g$ and $T_{2g}$ levels is called crystal field splitting energy and denoted either as $\Delta_o$ (the "O" stands for "octahedral") or 10 $Dq$, which could be calculated using the following equation:

$$Dq = \frac{ze^2r^4}{6R^3} \quad (1.2)$$

Where $Dq$ is the crystal field strength, $z$ is the anion valence, $e$ is the charge of an electron, $r$ is the radius of the $d$ wave function, and $R$ is the distance between the central ion and ligands. As shown in Equation (1.2), $Dq$ is inversely proportional to the bond length between the activator and ligands. The $Dq$ becomes weaker if the bond length increases and vice versa. The weak crystal field leads to a red shift in the photoluminescence spectrum.17
Figure 1.4 *d* orbital splitting in an octahedral crystal field (Central metal ion is represented as A, ligand is represented as L)

Normally, crystal-field levels are marked $^{2S+1}X$, where $S$ represents the total spin quantum number, $(2S+1) = 1, 2, 3, 4...$ are called singlets, doublets, triplets, quartets... And $X$ may be $a$ (no degeneracy), $e$ (twofold degeneracy) and $t$ (threefold degeneracy). The right-subscript $g$ means gerade and $u$ means ungerade. Gerade and ungerade designate the behaviour of the wavefunction under the operation of inversion and denote the parity (even or odd) of an orbital. The $u$ and $g$ labels are applicable only if the system possesses a centre of inversion and thus are used for the octahedral field, but not for the tetrahedral one.

### 1.1.1.2 Molecular orbital theory

Molecular orbital theory (MOT) is a semi-empirical method devoted to interpreting the energy-level structure of optical centers where the valence electron cannot be considered as belonging to a specific ion. In MOT, any electron in a molecule may be found anywhere in the molecule, since quantum conditions allow electrons to travel under the influence of an arbitrarily large number of nuclei, as long as they are in eigenstates permitted by certain quantum rules. It provides a global, delocalized perspective on chemical bonding. In our $\text{AL}_6$ reference center, this would mean that the valence electrons are shared by A and L ions. The approach is based on the calculation of molecular orbitals (MO) of the $\text{AL}_6$ pseudo-molecule, $\psi_{\text{MO}}$, constructed from various trial combinations of the individual atomic orbitals, $\psi_A$ and $\psi_L$, of the A and L ions, respectively. The molecular orbitals $\psi_{\text{MO}}$ of the center $\text{AL}_6$ are written in the general form:

$$\psi_{\text{MO}} = N(\psi_A + \lambda \psi_L)$$  \hspace{1cm} (1.3)
where $N$ is a normalized constant and $\lambda$ is a mixing coefficient. These MO functions are approximate solutions to the Schrödinger equation and their validity as wavefunctions for the $\text{Al}_6$ center is tested by calculating observable quantities with these MO functions and then comparing with experimental results.

MOT uses a linear combination of atomic orbitals (LCAO) to represent molecular orbitals resulting from bonds between atoms. And these are often divided into three types, bonding, antibonding, and non-bonding. A bonding orbital concentrates electron density in the region between a given pair of atoms, so that its electron density will tend to attract each of the two nuclei toward the other and hold the two atoms together. Electrons in this orbital spend most of their time in the region directly between the two nuclei (i.e. $\sigma$ or $\pi$ bonding). An antibonding orbital concentrates electron density on the side of each atom which is farthest from the other atom. It decreases the probability of finding an electron between the nuclei and results in a planar node of zero electron density halfway between the nuclei (Figure 1.5).

Without a buildup of negative charge between them, the nuclei repel each other, and no chemical bond is possible. The antibonding states correspond to the higher energy levels and are normally identified by an asterisk (i.e. $\sigma^*$ or $\pi^*$ antibonding). In non-bonding orbitals, electrons tend to be associated with atomic orbitals that do not interact positively or negatively with one another, and electrons in these orbitals neither contribute to nor detract from bond strength.\(^{19}\)

![Figure 1.5 MO diagram showing energy levels and electron density diagrams for atomic and molecular orbitals associated with hydrogenic 1s wave functions](image)
Figure 1.6 shows an example of the MO energy-level scheme for an octahedral $\text{AL}_6$ center, $[\text{Ti}^{3+}\text{O}_6]^{2-}$, the absorbing center in the Ti–sapphire crystal. $\text{A (Ti}^{3+})$ is a transition metal cationic ion (the left-hand side in Figure 1.6) and $\text{L (O}^{2-}$) is the anionic ions (the right-hand side Figure 1.6). The different MO and energy levels of the molecule are determined from the outer atomic orbitals 3d, 4s, and 4p of the ions $\text{A}$ and the p and s atomic orbitals of the ligand $\text{L}$ ions. Here, only linear combinations of the ligand s and p orbitals must be considered, giving rise to the $\sigma(s - p_z)$, $\pi(p_x, p_y)$ bonding energy levels and $\sigma^*, \pi^*$ antibonding energy levels of $\text{L}$ in Figure 1.6, where each arrow indicates a spin direction. Therefore, the last nonempty (partially filled) energy level of the $\text{AL}_6$ center is the antibonding $t_{2g}(\pi^*)$ level. When excited with the requisite amount of energy through high-frequency light or other means, electrons can jump to higher-energy molecular orbitals, leading to the so-called charge transfer (CT) transitions. Therefore, MOT could be used to interpret ultraviolet-visible spectroscopy (UV-VIS). Changes of the electronic structure of molecules can be seen by the absorbance of light at specific wavelengths which indicate the transition of electrons moving from one orbital at a lower energy to a higher energy orbital. Assignments can be made in absorption spectrum to these signals of electron transitions. Thus, MO theory is generally applied to interpretation of the so-called charge transfer spectra. However, for a great variety of centers in solids, crystalline field theory suffice to provide at least a qualitative interpretation of spectra.\(^{20}\)

![A schematic energy-level diagram for an octahedral AL₆ center within MOT. This diagram is constructed from the atomic levels of A and L. The filled and half-filled states (two possible opposite spins for each state) correspond to A = Ti³⁺ and L = O²⁻ ions\(^{20}\)](image)
1.1.2 Optical absorption and emission of phosphor

Not every possible electron transition is allowed for a photon absorption or emission, since these are governed by selection rules. Here are two important selection rules, spin selection rule and Laporte’s rule (parity selection rule).

❖ According to spin selection rule, electronic transitions are only allowed between levels with same spin states (ΔS=0).

❖ For parity selection rule, electronic (electronic-dipole) transitions between levels with same parity are forbidden, i.e. g→g or u→u.

Thus, electronic transitions like s→s, p→p, d→d, f→f, s→d or p→f etc. are forbidden whereas electronic transitions of s→p, p→d or d→f are allowed.

The characteristics of an optical absorption and emission band, i.e. narrow or broad, can be explained using the configurational coordinate diagram. To describe this coordinate, we need to consider the interaction between the central metal ion (activator) and the vibrations of its surroundings. Such a diagram shows the potential energy (E) curves of the luminescent center ion as a function of the metal-ligand distance (R), since R is the structural parameter which varies during the vibration. In principle, central metal ion is at rest and the surrounding ligands are moving in phase away from the metal ion and coming back which is known as stretching (or breathing) mode. In the system, the vibrational energy is quantized. The quantized vibrational states are indicated by the levels v_x. The horizontal lines in Figure 1.7a indicate the vibrational levels.

The optical absorption transition starts from the lowest vibrational level, i.e. v=0. Then the transition will end on the edge of the excited state parabola, where the vibrational levels of the excited state have their highest amplitude. And this transition corresponds to the maximum of the absorption band. It is also possible that there are transitions start at R values which is larger or smaller than R_0. For R> R_0, the energy difference of the transition will be less than that for R= R_0, and for R< R_0, it will be larger. This leads to the width of the absorption band (Figure 1.7b).

Now consider about another situation ΔR = 0, the absorption spectrum consists of a narrow line, corresponding to the transition from vibrational level v=0 to v′=0 (Figure 1.7c). This transition is called the zero-vibrational or no-phonon transition. In this case, the emission spectra consist of a narrow line at the same position with absorption.
Figure 1.7 (a) Ground state potential energy of a luminescent center in a crystal lattice with its associated vibrational states. (b) The optical absorption transition between two parabolas (ΔR>0) consist of a broad absorption band. (c) Energy diagrams of excitation and emission processes for displacement ΔR = 0. (d) Configurational coordinate diagram showing absorption transitions, emission transitions and Stokes’ shift between absorption and emission bands.

Figure 1.7d shows again the configurational coordinate diagram. For the moment we assume that there is an offset between the parabolas of the ground state and excited state, i.e. ΔR>0. As discussed before, the absorption occurs in a broad optical band and brings the activator in a high vibrational level of the excited state. Later, the activator returns first to the lowest vibrational level within the excited state by losing some energy to the surroundings. This process is called relaxation, there occurs usually no emission. At this point, from the lowest vibrational level of the excited state the system can returns to the ground state under emission of radiation. Therefore, the energy required to excite the system (absorption) is greater than the energy of emission. The energy difference is called Stokes shift.

If the two parabolas have same shape, the amount of energy lost in the relaxation process is $Sh\nu$ per parabola, where $\nu$ is the spacing between two vibrational levels and $S$ is usually an
integer. The Stokes shift equal to $2S\hbar\nu$. The constant $S$ is called the Huang-Rhys coupling constant. It is proportional to $(\Delta R>0)^2$ and represent the strength of the electron-lattice coupling. Obviously, the larger the value of $\Delta R$ is, the greater the Stokes shift and broader the optical bands involved. Normally, if $S < 1$, it indicates weak coupling, if $1 < S < 5$, intermediate coupling, if $S > 5$, strong coupling.

As reported in previous works, the Huang–Rhys factor be extracted by fitting the temperature dependent full-width at half maxima (FWHM) of photoluminescence peaks using the following equation:

$$\text{FWHM} = 2.36\sqrt{S\omega_{\text{phonon}}\sqrt{\coth\left(\frac{\hbar\omega_{\text{phonon}}}{2k_B T}\right)}}$$

(1.4)

where $S$ is the Huang-Rhys factor, $\hbar\omega_{\text{phonon}}$ is the phonon frequency, $k_B$ is Boltzman constant. The Huang-Rhys factor is associated with the displacement of the equilibrium positions of the nuclei upon exciting the chromophore, which reflects the strength of the linear electron-phonon coupling. And the larger the HR factor, the stronger the coupling, and the more likely self-trapped excitons (STE) is to occur.

### 1.1.3 Jahn–Teller effect

If $R$ denotes the distance between the central metal ion and the ligands, the absorption-emission cycle can be visualized as follows: absorption occurs without change of $R$, and is followed by expansion of the luminescent center till the new equilibrium distance ($R + \Delta R$) is reached; subsequently emission occurs without change of distance followed by a contraction $\Delta R$ till the equilibrium distance is reached (Figure 1.8). This justified approximation is the so-called symmetrical stretching (or breathing) mode. However, this description is often not correct, because the excited state may be distorted relative to the ground state.

![Figure 1.8 Schematic diagram for breathing mode of electronic transitions](image)

#### 1.1.3.1 The first-order Jahn-Teller distortion

As mentioned in Crystal Field Theory above, for a given octahedral complex, the five degenerate $d$ orbitals are split into two degenerate sets, $T_{2g}$ ($d_{xz}$, $d_{yz}$, $d_{xy}$) and $E_g$ ($d_{z^2}$ and $d_{x^2-y^2}$)
when constructing a molecular orbital diagram. But actually, when a molecule possesses a degenerate electronic ground state, it will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy which is otherwise known as Jahn-Teller distortion.\textsuperscript{27–29} The octahedral complex will either elongate or compress the z ligand bonds as shown in Figure 1.9 below:

\begin{center}
\includegraphics[width=0.5\textwidth]{fig19.png}
\end{center}

\textit{Figure 1.9 Jahn-Teller distortion for an octahedral complex under axial compression and elongation along the z-axis (tetragonal elongation, left side and tetragonal compression, right side).}

For elongation Jahn-Teller distortions, assume that the two ligands in z direction are moved away from the central metal ion, the electric field experienced by d orbitals pointing in z direction is weaker and thus ultimately, they are destabilized less (lowering in energy) while the orbitals without a z component are destabilized (higher in energy). The $d_{xy}$ and $d_{x^2−y^2}$ orbitals have greater overlap with the ligand orbitals, which results in the orbitals being higher in energy.

The effect would be opposite for compression Jahn-Teller distortions. If the ligands in z direction get closer, the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals without a z component, while the orbitals with a z component are destabilized (higher in energy). This is due to the z-component d orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy.

These two distortions are dictated by the amount of orbital overlap between the metal and ligand. Thus, the distortions vary greatly depending on the type of metal and ligands. In general, the stronger the metal-ligand orbital interactions are, the greater the chance for a Jahn-Teller effect to be observed\textsuperscript{30}.
1.1.3.2 The second order Jahn-Teller distortion

The pseudo Jahn–Teller effect (PJTE)\textsuperscript{29}, occasionally also known as second-order JTE, is the most important extension of the original JT theorem. It was shown that the spontaneous distortion may also take place when two or more electronic states are not exactly degenerate but are very close in energy (pseudodegenerate)\textsuperscript{31}. It served as a trigger of a much more important conclusion that sufficiently strong vibronic coupling between any two electronic states (often ground and excited) with any energy gap between them may lead to instability and distortion of the polyatomic configuration\textsuperscript{32}. The pseudo-Jahn–Teller effect is the only source of instability and distortions of high-symmetry configurations of polyatomic systems in nondegenerate states, and it contributes essentially to the instability of degenerate states\textsuperscript{29,32–34}. The second-order Jahn-Teller effect can lead to very large distortions of molecular geometry, or even complete dissociation of a molecule\textsuperscript{35}.

Electrons in the degenerate states are de-localized to the greatest possible extent. However, under Jahn-Teller effect, distortion forces the electrons to localize more in the MOs that are stabilized\textsuperscript{36}.

1.1.4 Ions with $s^2$ Configuration

Here, an introduction for term symbols will be firstly provided. For the free ion, the different energy levels are marked $^{2S+1}L_J$, where $S$ represents the spin quantum number, and $L$ is the orbital quantum number. Energy states for which $L = 0, 1, 2, 3, 4 ...$ are known as $S, P, D, F, G ...$ terms respectively. The value of $J$ as a right-subscript is total angular momentum quantum number, e.g., $^3P_0$ (‘triplet P zero’) denote $L=1, (2S+1)=3$ (i.e. $S=1$) and $J=0$\textsuperscript{19}. The degeneracy of these levels i.e. $2L+1$ may be lifted by the crystal field.

Ions with $s^2$ outer electronic configuration show strong optical absorption in the ultraviolet range due to a characteristic $s^2→s^1p^1$ transition\textsuperscript{18,37–39}. The ground state of $s^2$ ion is $^1S_0$, and the two lowest-energy excited states are triplet $^3P$ and singlet $^1P$. Due to the spin-orbit interaction, the triplet state split into the $^3P_0, ^3P_1$, and $^3P_2$ states. In view of the transition rule, only $^1S_0→^1P_1$ transition is allowed. However, $^1S_0→^3P_1$ transition can be partially allowed due to a spin-orbit coupling for heavy atoms. In the crystals, the forbidden $^1S_0→^3P_2$ transitions also become partly allowed due to vibronic mixing of the $^3P_2$-related state with the triplet or singlet states by non-totally symmetric lattice vibrations\textsuperscript{38,40}. Thus, the intensity of this transition should increase with temperature. The $^1S_0→^3P_0$ transitions are totally forbidden.
Therefore, in the crystal, the absorption (excitation) bands labelled as A, B, and C which corresponding to the electronic transitions from the ground $^1S_0$ level of a free $s^2$ ion to the excited $^3P_1$, $^3P_2$, and $^1P_1$ levels respectively, can be observed (Figure 1.10).

![Energy level schemes for $s^2$ ion](image)

**Figure 1.10 Energy level schemes for $s^2$ ion**

Here, an example is absorbance of Sb$^{3+}$ doped Cs$_2$NaInCl$_6$ and Rb$_3$InCl$_6$ in Figure 1.11a. A number of near-UV absorption features are observed for both Cs$_2$NaInCl$_6$ and Rb$_3$InCl$_6$ as soon as Sb$^{3+}$ ions are incorporated. These features are characteristic of $5s^2 \rightarrow 5s^1p^1$ absorption transitions of the [SbCl$_6$]$^{3-}$ octahedra. The broad absorption centered $\sim 260$ nm is assigned as the spin and parity allowed $^1S_0 \rightarrow ^1P_1$ transition (C band). A weak peak at $\sim 280$ nm is assigned to the parity and spin forbidden $^1S_0 \rightarrow ^3P_2$ transition (B band), which appears because vibronic coupling and spin–orbit coupling lead to relaxation of the selection rules. Lastly, a doublet with peaks at $\sim 320$ and $\sim 340$ nm corresponds to the $^1S_0 \rightarrow ^3P_1$ transition (spin forbidden, parity allowed) is the A band. And this transition is partially allowed caused by spin–orbit coupling between $^1P_1$ and $^3P_1$ states. The splitting of absorption peak is due to a dynamic Jahn–Teller (JT) distortion of the excited state, which couples to lattice vibrations.\(^{41}\)

![Absorption plots](image)

**Figure 1.11 Absorption (via Kubelka-Munk transformation) of (a) Sb$^{3+}$ doped Cs$_2$NaInCl$_6$ and Sb$^{3+}$ doped Rb$_3$InCl$_6$. (b) Comparison of Rb$_3$InCl$_6$ with (blue) and without Sb$^{3+}$ (black) doping\(^{41}\)**
1.1.5 Nonradiative Transitions

The most important nonradiative de-excitation process that competes with radiative de-excitation is that due to multi-phonon emission\textsuperscript{16}. The down relaxation between different vibrational levels mentioned above is one kind of multi-phonon de-excitation. Let us consider another case from the configurational coordinate diagram in Figure 1.12. If the exciton-phonon coupling is very strong (lager Huang–Rhys parameter), it may lead to the crossover of the two parabolas locates at lower energy than vibrational level. Consequently, via the crossing the relaxed excited state is possible to return to the ground in a nonradiative manner by the phonon-assisted pathway. Herein, this model can also provide explanation for the thermal quenching of luminescence (Figure 1.12b). The energy difference (height) between the crossover and the excited-state minimum defines the energy barrier\textsuperscript{42}. If the temperature is high enough, thermal population of the level at crossover can also be populated which can be easily annihilated by the phonon-assisted pathway.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{configurational_coordinate_diagram.png}
\caption{Configurational coordinate diagram illustrating nonradiative transitions (a) and thermal quenching(b).}
\end{figure}

1.2 Luminescent semiconductors

1.2.1 Semiconductors

In semiconductors, there is an energy gap \( E_g \) between the filled valence band and the empty conduction band. Here, we consider an example of energy band formation in Si (most frequently used material in semiconductors). Si atom has \( 3s^23p^2 \) outer shell, the \( 3s \) and \( 3p \) orbitals, \( \psi (3s), \psi (3p_x), \psi (3p_y) \) and \( \psi (3p_z) \) are close in energy and thus can hybridize to form \( sp^3 \) orbitals, i.e. \( \psi_{hyb} \) as shown in Figure 1.13a and b. Given that there are four electrons, a total of four half occupied \( sp^3 \) hybrid orbitals are formed. Therefore, when five Si atoms
approach each other, one of them will overlap its four $sp^3$ hybrid orbitals with that of other four Si atoms which forms four bonds in tetrahedral directions.

Figure 1.13 (a) Isolate Si atoms showing the outer shell orbitals (two electrons in the 3s and two electrons in the 3p orbitals). (b) When Si is about to bond, four hybridized orbitals, $sp^3$, are formed and directed toward the corners of a tetrahedron which indicate each hybrid orbital is aimed to as far away from the others as possible. (c) Forming crystals by bonding silicon atoms.\(^{43}\)

There are two ways the hybrid orbital $\psi_{hyb}$ can overlap with the neighboring Si atom which form two types of molecular orbitals: a bonding ($\sigma$) and an anti-bonding ($\sigma^*$) orbital, with energy $E_B$ and $E_A$, respectively. Since each Si atom will contribute one electron to the bond, each Si-Si bond corresponds to a paired electrons in bonding orbital. In the solid, there are $N$ ($\sim 5 \times 10^{22} \text{cm}^{-3}$) Si atoms and the nearly same number of bonding orbitals. The interaction between bonding orbitals causes that the $E_B$ level is split into $N$ levels, and forming an energy band, called valence band. Similarly, the anti-bonding orbitals can interact to form an energy band, called conduction band. Here, the valence band is completely full of electrons while the conduction band is completely empty, and these two bands are separated by a forbidden energy gap, called band gap, $E_g$.\(^{43,44}\) The formation of energy bands in Si crystal can be seen from Figure 1.14. Further, the lowest unfilled energy level of conducting is called band Conduction Band Minimum (CBM) while the highest filled energy level of valence band is called Valence Band Maximum (VBM).

Figure 1.14 (a), Si atom with 3s\(^2\)3p\(^2\) outer shell. (b), $sp^3$ hybrid orbitals. (c) The hybrid orbitals form $\sigma$ and $\sigma^*$ orbitals. (d) Formation of valence and conduction band.\(^{43}\)
1.2.2 Recombination in semiconductors

Electrons can be excited from the valence band to the conduction band by either thermal excitation or upon photon absorption. When the electron returns to the valence band the energy is released either by phonons (heat) or as photons.

During a photon absorption or emission process in semiconductors, energy and momentum must be conserved. In direct band gap semiconductors, it does not involve any phonons since k-vectors of the CBM and the VBM are same as shown in Figure 1.15. In an indirect band gap semiconductor, to conserve momentum, the photon absorption process must involve either absorb (indicated by a “+”) or emit (indicated by a “−”) a phonon to change momentum state, while the PL process needs the emission of a phonon.\footnote{45}

The excited electron and hole will not remain in their initial excited states for very long, instead, they will relax very rapidly to the lowest energy states within their respective bands by emitting phonons. This process is called thermalization which typically occurs within femtoseconds (fs).\footnote{46} When the electron or hole finally arrives at the bottom of the conduction band or top valence band, it creates the electron-hole pair, called exciton. Recombination is the annihilation of an electron and a hole. Four recombination fundamental mechanisms can be distinguished: radiative recombination, Shockley-Read-Hall (SRH) recombination, Auger recombination and surface recombination, which were all depicted schematically in Figure 1.16.\footnote{47} Radiative recombination is also called band to band recombination, it happens if the electron-hole pair recombines and emits a photon. In (SRH) recombination, some defect

\[Figure\ 1.15\ Schematic\ of\ E-k\ diagrams\ for\ the\ interband\ photoluminescence\ processes\ in\ a\ direct\ gap\ material\ (left)\ and\ an\ indirect\ gap\ material\ (right),\ where\ E\ and\ k\ are\ the\ kinetic\ energy\ and\ wave\ vector\ (or\ ”momentum\ vector”)\ respectively.\footnote{45} \]
levels are introduced between the band edges, which can trap charges and become a recombination center. The energy is either emitted by a phonon or a photon. Auger recombination is a three-particle process. An electron transfers its energy to another electron which is subsequently elevated to a higher energy state in the conduction band and later relax to the conduction band edge by emitting phonons. Surface recombination happens via one or more states within the band gap which was created by dangling bonds or defects that are present at the surface. A charge carrier reaching a surface and hops from state to state releasing its energy by phonon emission.

![Radiative Recombination, SRH Recombination, Auger Recombination, Surface Recombination](image)

*Figure 1.16 Schematic illustration of the fundamental recombination mechanisms.*

### 1.2.3 Self-trapping exciton (STE)

In crystal, charge carriers can couple to a soft lattice, inducing a strong local deformation of the lattice, an exciton may be localized by its own lattice distortion field, i.e. self-trapped exciton. As described by Mott and Stoneham, polaron is classified into two types according to its scale and potential well depth: “dielectric polarons” which result from the Coulomb interaction of electrons or holes in polar lattice; and “molecular polarons” in which the essential interaction is short-range forces like chemical bonding. STEs are similar to small polarons, in which the large associated lattice deformations is primarily confined about a single lattice site.

In polar materials, carriers can easily be self-trapped near the defects and also in a defect-free deformable lattice. Smith and Karunadasa described intrinsic self-trapping, defect trapping and extrinsic self-trapping vividly by a hard ball (electron/hole/exciton) dropping on a pliable rubber sheet (a deformable lattice) as shown in Figure 1.17. For intrinsic self-trapping, in the absence of permanent material defects, carriers are self-trapped at the
deformed lattice sites which are induced by significant coupling between the exciton and the lattice. This is different from defect trapping where the distortion existed prior to contact with the carriers. However, the local heterogeneity of lattice caused by impurities or defects could create short-range and/or long-range potentials thus enhance self-trapping that is extrinsic mechanism.\textsuperscript{50,51} From another perspective, STEs could be viewed as “excited state defects”, as they exist only upon excitation, and the lattice distortion disappears following decay to the ground state.\textsuperscript{52} Remarkably, the Huang-Rhys factor $S$ which describe the electron–phonon coupling strength can be used to indicate the soft crystal nature of materials, and the softer lattice could more easily generate the STEs.\textsuperscript{53}

![Figure 1.17 Schematic illustration of (a) Intrinsic self-trapping, (b) trapping at permanent defects and (c) self-trapping induced by permanent defects.\textsuperscript{50}](image)

The effect of STEs could be observed spectroscopically. Specifically, STEs could lead to broadband emission with a large Stokes shift, while free excitons often have sharp and narrow PL band with small Stokes shift. Meanwhile, STE-related emissions usually exhibit relatively long lifetime (time scale of microsecond - millisecond)\textsuperscript{54}, which is significantly different from the free/bound excitons (nanosecond scale).\textsuperscript{55}

### 1.3 White light emission

#### 1.3.1 Single-component white light emitting from lead halide perovskite

In the past few years, metal halide perovskites (MHPs) attracted significant attention not only in potential photovoltaic applications, but also in other optoelectronic applications, such as light-emitting diodes (LEDs)\textsuperscript{56}, X-ray scintillators\textsuperscript{57} and photodetectors\textsuperscript{58}. For broadband white light emission, MHPs with various structural dimensionality (0D, 1D, 2D and 3D) have been
reported. For instance, Teunis et al. reported the 0D intrinsic white-light emitting perovskite nanoclusters (PNCs) with quantum yields \(\sim 12\%\). Ultrasmall (\(\sim 1.5 \text{ nm} \)) methylammonium lead bromide (MAPbBr\(_3\)) PNCs were prepared by colloidal synthetic method. PL emission displayed a combination of sharp band-edge emission (peak at 403 nm) and broadband emission (peak at 512 nm) as shown in Figure 1.18a. The white light emission was attributed to radiative recombination of excitons at surface-related mid-gap trap-states since L-type ligands and their interaction with Pb\(^{2+}\) in PNCs lead to formation of antibonding orbitals below the conduction band of PNCs. The mechanism of the broad PL emission in 1D and 2D perovskite materials was generally ascribed to self-trapping of excitons or electrons/holes. Ma et al. synthesized one-dimensional (1D) organic lead bromide perovskites Ca\(_{2}\)H\(_{14}\)PbBr\(_4\) and this colorless needle-shaped crystal showed strong bluish white light emission upon UV irradiation. Such a 1D structure could be regarded as quantum wires system in which the inorganic edge sharing octahedral lead bromide chains act as semiconductor wires and the organic cations act as insulator barriers. The photoluminescence quantum efficiencies of the bulk single crystals could achieve to 20\% as the unique 1D structure enables strong quantum confinement with the formation of self-trapped excited states that give efficient white light emissions. Karunadasa et al. first described broadband white-light emission from the two-dimensional (2D) lead-halide perovskites: \((\text{N-MEDA})\text{PbBr}_4\) and \((\text{EDBE})\text{PbX}_4\) \((\text{N-MEDA} = \text{N}\(^1\)-methylethane-1,2-diammonium; \text{EDBE} = 2,2'-\text{ethylenedioxy}bis(ethyl-ammonium); \text{X} = \text{Cl and Br})\) and the most efficient photoluminescence quantum efficiency (PLQY) is 9\%. They noted that the broadband Stokes-shifted emission originated from a photogenerated energy distribution of STE states. Photogenerated free carriers typically first formed free excitons, which then relaxed into STEs with an associated surrounding lattice deformation due to strong electron–phonon coupling\(^{46}\). Compare to 3D systems, potential barrier separating the free exciton and STE in low dimensional systems (1D or 2D) is much lower,\(^{49}\) and thus, the STE formation typically happens promptly. In addition, the permanent lattice defects (such as vacancies) or dopants may also aid the self-trapping process and further widen the emission\(^{59}\). In the case of 2D perovskite PEA\(_2\)Pbl\(_4\) (PEA = phenylethylammonium), the exciton self-trapping never occurs in its pure state. However, by doping isoelectronic Sn, local potential wells were created because of local heterogeneity of the lattice which initiated the localization of excitons and further induce the large lattice deformation around the impurities to facilitate exciton self-trapping\(^{60}\).
Smith et al. denote that the lattice distortions could be caused not only by intra-octahedral asymmetry but also inter-octahedral tilting which contains in-plane component and out-of-plane component.\(^{61}\) This inter-octahedral distortion is induced by steric and hydrogen-bonding interactions from the organic cations and is predominantly observed in two-dimensional halide perovskites.\(^ {62}\) Compared in-plane and out-of-plane views of the inorganic sheets in (BA)\(_2\)PbBr\(_4\), (HIS)PbBr\(_4\), and (AEA) PbBr\(_4\), they point out that the out-of-plane distortion is the key structural parameter correlating with the broad emission since it could enhance the localization of the in-plane confined excitons.\(^ {63}\) (C\(_6\)H\(_{11}\)NH\(_3\))\(_2\)PbBr\(_4\) was also mentioned as it shows broadband emission but with no out-of-plane distortion because it is a polar material which exhibits much high degree of electron–phonon coupling.

Yan et al. elucidate that it is the electronic dimensionality rather than structural dimensionality determine the formation of STEs and broadband emission. They also indicate only the STE with Jahn–Teller-like octahedral distortion is responsible for the observed broadband emission.\(^ {63}\) They find that there are two types of STE structures in MHPs, i.e., Jahn–Teller-like distortion (STE1) and non-Jahn–Teller-like distortion (STE2). For 2D material (NMEDA)PbBr\(_4\), the structure of STE1 is shown in Figure 1.19b, the [PbBr\(_6\)] octahedron with elongation of the two axial Pb–Br bonds and contraction of the four equatorial Pb–Br bonds localize the trapping electron and hole in single octahedron. Thus, compare with STE2, electron–hole orbital overlap of STE1 is larger. From the configuration coordinate diagram of STE2, it obviously shows a pathway for nonradiative transition. Therefore, enhancing the formation of radiative STE1 and suppressing the formation of the nonradiative STE2 are feasible approaches for improving the broadband emission quantum efficiencies.
1.3.2 Double perovskite single-component white light emitter

For low dimensional (0D, 1D, 2D) single materials with white light emission, organic cations play a key role on reducing dimensionality (break octahedral connection networks), facilitating octahedral distortion etc., whereas the organic part also cause instability problem under certain unfavorable conditions (moisture, UV light, oxygen, temperature etc.), let alone Pb toxicity issue. These are two main challenges for MHPs application in photovoltaics. In recent years, double perovskites have been exploited to substitute the two divalent cations Pb\(^{2+}\) in single perovskite by a combination of a monovalent and trivalent cation, namely A\(^{2+}\)B\(^{3+}\)X\(^{6-}\) which maintain the 3D perovskite structural framework. Strikingly, these lead free inorganic double perovskite materials have shown an excellent stability in ambient atmosphere, and remarkable properties used as single-source emitter for warm white light in LED.

Based on Cs\(_2\)AgInCl\(_6\), Tang’s group first reported the 3D alloyed double perovskite Cs\(_2\)(Ag\(_{0.60}\)Na\(_{0.40}\))InCl\(_6\): 0.04% Bi as single component white light emitting phosphors and diodes with quantum efficiency as high as 86%. This broadband white emission is ascribed to self-trapped excitons that originate from the Jahn–Teller distortion of the [AgCl\(_6\)] octahedron in the excited state. Cs\(_2\)AgInCl\(_6\) possesses very low PLQY (<0.1%), with alloying sodium cations into Cs\(_2\)AgInCl\(_6\), parity-forbidden transition was broken and electronic dimensionality was reduced which brought the increase in photoluminescence efficiency. Regarding to the effect of Bi\(^{3+}\) on the remarkable enhancement for PLQY, they explained that Bi doping
passivates defects of In\textsuperscript{3+} vacancy and suppresses non-radiative recombination loss. In
addition, Bi doping introduces a shallow state right above the valence band maximum (VBM)
and forms nano electronic domains which trap holes and furthermore, promotes exciton
localization. Herein, as a ns\textsuperscript{2} ion, the role Bi plays is similar to another Bi doped material whose
host is Cs\textsubscript{2}SnCl\textsubscript{6}, a vacancy ordered double perovskite\textsuperscript{68}. It could be observed from Figure
1.20a that, for host material Cs\textsubscript{2}SnCl\textsubscript{6}, Bi doping gives rise to an additional absorption peak
around 375 nm and an emission spectrum centered around 454 nm\textsuperscript{69}. For the case of
Cs\textsubscript{2}AgInCl\textsubscript{6}, Bi doping also leads to a new absorption with peak at 372 nm but a broadband
emission in visible range\textsuperscript{13}. Here, both the new optical absorption with a peak between 360
and 400 nm is attributed to \textsuperscript{1}S\textsubscript{0}→\textsuperscript{3}P\textsubscript{1} transition of the Bi\textsuperscript{3+} ion and thus the emission obtained
is assigned to the \textsuperscript{3}P\textsubscript{1}→\textsuperscript{1}S\textsubscript{0} transition. In undoped Cs\textsubscript{2}SnCl\textsubscript{6}, the VBM is mostly derived from Cl
3p orbitals, while the CBM is contributed by antibonding states of Sn 5s and Cl 3p orbitals.
Regarding to Bi-doped Cs\textsubscript{2}SnCl\textsubscript{6}, Bi\textsuperscript{3+} substitutes the Sn\textsuperscript{4+} site with creation of the Cl\textsuperscript{−} vacancy
and forms a defect complex [BiCl\textsubscript{5}]\textsuperscript{2−}. Bi\textsuperscript{3+} 6s\textsuperscript{2} orbitals hybridize with Cl 3p orbitals which create
a fully occupied defect band (VBM’) at 0.99eV above the VBM (Figure 1.20d). The energy of
Bi 6s orbital is lower than the Sn 5s orbital, thus CBM is almost not affected. Thus, this VBM’
is responsible for the lower energy optical absorption and a reduced bandgap in Bi\textsuperscript{3+} doped
Cs\textsubscript{2}SnCl\textsubscript{6}\textsuperscript{69}. 

![Graph](image-url)
In fact, for broadband white emission, the mechanism of STEs formation, in particular the processes and dynamics of excitons associated with the efficient emission are still unclear. In this work, single-component white light emitting materials Cs$_2$Na$_{1-x}$Ag$_x$In$_{1-y}$Bi$_y$Cl$_6$ were synthesized in a simple procedure whose PLQY almost achieves unity. Here, it is aimed to expand the understanding on the emission mechanism for white light as well as the insights in the rational design of hosts, dopants, and co-dopants, also for their potential applications in LED. This part will be further elaborated in Chapter 3 and Chapter 4. In the next chapter, some basic knowledge for double perovskite will be introduced which includes the crystal structure, synthesis approaches and characterization methods.
CHAPTER 2  Understanding double perovskites

Hybrid halide perovskites have been a rising star in the field of optoelectronics\textsuperscript{71–76}. However, the poor long-term stability and toxicity of Pb are two critical issues which may hinder the eventual commercialization of hybrid halide perovskite-based optoelectronic devices. Many efforts have been committed to search for non- or low-toxicity and air-stable perovskite-based analogues with a similar electronic configuration. The isoelectronic s\textsuperscript{2}p\textsuperscript{6} elements in the same group IV are thus the most obvious candidates to replace Pb. However, Sn and Ge suffer from instability and oxidization since they are more stable in a 4+ oxidation state instead of 2+ state which cause Sn/Ge ABX\textsubscript{3} perovskites show the formation of Sn/Ge lattice vacancies\textsuperscript{77}. Later, the combinations of monovalent and trivalent cations to replace divalent cations Pb\textsuperscript{2+} in single perovskite were proposed which are the so-called double perovskites, forming structure as A\textsubscript{2}B\textsuperscript{+}B\textsuperscript{3+}X\textsubscript{6} (A = mono-cation, X = halide). Double perovskites exhibit extended three-dimensional structures resembling ABX\textsubscript{3} perovskites while permitting a wide variety of cations to be incorporated into the octahedrally coordinated B\textsuperscript{+}/B\textsuperscript{3+} site. This enables access to a potentially large number of alternative compositions and electronic structures, which are only beginning to be explored. Besides, it is important to study the systematic change of the size, valence, and electronic configuration of the constituent ions so as to investigate the effects of these parameters on magnetic, electrical properties and crystal chemistry\textsuperscript{78}.

In this chapter, I will firstly introduce the crystal structure of double perovskite. Then the synthesis method of double perovskite will be presented which include crystal, powder and thin film. In the third part, I will talk about the characterization of the crystal structure and photoelectronic properties.
2.1 Crystal structure of halide double perovskites

2.1.1 Structural diversity of halide double perovskite

Halide double perovskites (A$_2$B$^+$B$^{3+}$X$_6$) have been reported to possess highly symmetric face-centered cubic structures, belonging to Fm$\overline{3}$m space group, consisting of a 3D framework of corner connected octahedra, with A$^+$ ions occupying the octahedral external cavities in the framework. Different from hybrid halide perovskites where the perovskite structure is obtained by just Pb$^{2+}$ centered octahedron, the halide double perovskite structure is built of alternating B$^+$ and B$^{3+}$ centered octahedrons of [B$^+$Cl$_6$]$^{5-}$ and [B$^{3+}$Cl$_6$]$^{3-}$ in a 3D framework known as rock salt ordering. The crystal structures of the hybrid halide perovskites and halide double perovskites are shown below in Figure 2.1.

![Figure 2.1. Schematic illustration of B$^+/B^{3+}$ cation substitution from hybrid halide perovskites (APb$^{2+}$X$_3$) to double perovskites (AB$^+$$B^{3+}$X$_6$). The A$^+$, B$^{2+}$, B$^+$, B$^{3+}$ and X$^-$ are represented by cyan, grey, pink, blue and brownish red.]

Considering the crystal structure of halide double perovskites, the related compounds have been known for many years with the name of "elpasolites". It is reported that at least 350 different elpasolites have been synthesized$^{79}$. After doing a survey of the literature on elpasolites, Giustino and Snaith$^{80}$ highlight all the elements of the periodic table which belong to known halide elpasolites in Figure 2.2. Based on this table, Wu et al. added that Cu$^+$-based metal halides have desirable bandgaps ($\sim$1eV$^{81}$) for photovoltaic applications. Although [CuCl$_6$] octahedra with sixfold coordination is not energetically favorable comparing forming [CuCl$_4$] tetrahedra$^{82}$, it can also be stable in several strict conditions$^{83}$. In this work, I also recognized this possibility and it will be discussed in next chapter.

Halide double perovskite is a big family worthy of further exploration. It has more flexibility to engineer the electronic band since all the A, B$^+$, B$^{3+}$, X sites may be substituted while
incorporated into the structure. Especially, the tunability of $B^+ / B^{3+}$-site and related $BX_6$ octahedron can effectively change the band gap parity symmetry and direct vs indirect nature. Theoretical calculations indicate halide double perovskites have a loose lattice, which guarantees its promising application in the field of optoelectronic. So far, halide double perovskites have been applied in solar cells, light-emitting devices, photodetectors, photocatalysis, scintillators and room-temperature ferromagnetic semiconductors exhibiting impressive performance.

Figure 2.2. Elements forming halide double perovskites with composition $A_2B^+B^{3+}X_6$. Only structures that crystallize in the space group $Fm-3m$ at room temperature are considered. Note that $Cu^+$ can also form stable halide double perovskites, which is marked with brownish red.

2.1.2 “Disorder” in the ordered double perovskite

The study of oxide double perovskites $A_2B'B''O_6$ was initiated in the early 1950s. And from the late 1980s, oxide double perovskites have again gained attention for their outstanding performance on superconductivity above the boiling point of liquid nitrogen, $77 \text{ K}$. For oxide double perovskites, order-disorder effects are commonly found when the charge difference between $B'$ and $B''$ is two or less. Interchanging $B'$ and $B''$ ionic positions will create antisite disorder defects, which may affect the magnetic and magneto-transport response of double perovskite oxides. Such as $Sr_2FeMoO_6$, which are known to have interesting properties of ferromagnetism, ferroelectricity and superconductivity, antisite defects can occur by Fe/Mo cationic disorder which may influence the electronic structure and bring about a decrease in the magnetization. Therefore, many researchers have been focused on studying the detailed nature of cationic disorder for a microscopic understanding of the unusual properties of oxide double perovskites.
Meneghini et al. noted an apparent conflict between results of synchrotron radiation based x-ray diffraction (XRD) data and x-ray absorption fine structure (XAFS) experiments when they studied the degree of Fe/Mo order in Sr$_2$FeMoO$_6$. For the same sample disorder, the XAFS suggested extensive disorder while the XAFS indicated nearly perfect ordering. They pointed out that the of B’/B” disorder defects could not be considered as only a random disorder throughout the lattice (Figure 2.4a). The defects may segregate as shown in Figure 2.4b and Figure 2.4c. The boundaries between the ordered antisite segregation regions and the original ordered lattice are known as the antiphase boundaries. In the segregation regions, the so-called defects recover the perfect periodicity of the original lattice and such ordered patches have properties almost identical as the original ordered lattice. So, it is important to learn both the short- and long-range order features for understanding the properties of oxide double perovskites.

Zagorodniy et al. studied chemical disorder of Pb(Fe$_{1/2}$Sb$_{1/2}$)O$_3$ by combining XRD and NMR. They indicated that an effective order parameter $s_{eff}$ which can be extracted from XRD while the volume fraction of ordered (or partly ordered) regions $s'$ can be estimated from the NMR.
spectra. Later, according to \( s_{\text{eff}}^2 = s^2 s' \), the long-range order parameter \( s \) could be determined\(^{106}\).

To visualize the atomic structure, Lim et al. use high-angle annular dark-field scanning-transmission electron microscopy (HAADF-STEM) to study antisite defects in Re-excess \( \text{Sr}_2\text{FeReO}_6 \) (SFRO-xRe) and \( \text{Sr}_2\text{CrReO}_6 \) (SCRO-xRe) along the \([110]\) zone axis\(^{107}\). Sequential arrangements of \( \text{Sr}-\text{Fe}-\text{Sr}-\text{Re}-\text{Sr} \) atoms are clearly displayed in the \([110]\) projection in Figure 2.5a. It could be obviously to observe the antiphase boundary in Figure 2.5b for 5 mol \% excess Re, i.e. SFRO-5Re. However, the size of clustered AS defects decreased when 15 mol \% excess Re was added (Figure 2.5c).

There have been lots of reports on B cation order/disorder for oxide double perovskites, however, halide double perovskites have also attracted substantial interest in this area of study. Recently, several works revealed that, for halide double perovskites, the B cation order/disorder could change the band structure\(^{108}\) and induce deep gap states because of the formation of antisite defects in the crystal lattice\(^{109}\). Solid-state nuclear magnetic resonance (NMR) spectroscopy is a powerful analytical tool to characterize atomic-level short- and medium-range structure\(^{110-114}\). With the help of NMR, Michaelis’s group unraveled the complex short- and medium-range structure of Cu(II)-Doped \( \text{Cs}_2\text{SbAgCl}_6 \)\(^{115}\) and alloyed \( \text{Cs}_2\text{Bi}_{1-x}\text{In}_x\text{AgCl}_6 \) halide double perovskites.

The degree of B'/B'' ordering can be qualitatively determined in the cubic double perovskite structure by comparing the diffracted intensity ratio \( I(111)/I(200) \) of XRD.\(^{116}\) In halide double perovskite, the two different (B' and B'') cation positions adopt a rock-salt arrangement. For simplicity, A-site cation and halogen are not shown in the B-cation sublattice in Figure 2.6b, in which the \([111]\) B planes are highlighted with fluorescent green and pink(Figure 2.6c). We
can see every other (111) plane belongs to B' sublattice (in pink) but the remaining (111) planes belong to B'' sublattice (in fluorescent green). The (200) planes are highlighted with fluorescent blue\textsuperscript{117} (Figure 2.6d).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure26.png}
\caption{(a), Crystal structure and (b), B-cation sublattice of rock-salt-ordered double perovskites $A_2B'B''X_6$. (c), (111) planes and (d), (200) planes in double perovskite crystalline structures.}
\end{figure}

Tang's group evaluate the degree of ordering in $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{InCl}_6$ by comparing the XRD diffracted intensity ratio $I(111)/I(200)$\textsuperscript{23}. The (111) reflection is a superstructure peak associated with the B'/B'' alternative ordering while each (200) plane contains both B'(I) and B''(III) cations and hence its diffraction peak intensity is insensitive to this ordering in the case of doping.

### 2.2 Synthesis of double perovskite

Due to the quaternary nature, synthesis of double perovskite is apparently more complex. Especially, the preparation of high-quality thin films is challenging because of lower precursor solubility. In the following section, several most commonly used synthetic approaches will be introduced to prepare crystals (single crystals, polycrystalline powders and nanocrystals) or
fabricate thin films by using solution synthesis/ solid state synthesis or solution deposition/vapor deposition, respectively, depended by material composition.

2.2.1 Synthesis of double perovskite single crystals

2.2.1.1 Hydrothermal method (high pressure)

The growth of large-size high-quality perovskite single crystals are mostly reported to be synthesized with hydrothermal reaction technique\textsuperscript{118–121}. Ahn et al. reported highly crystalline Cs\textsubscript{2}AgBiBr\textsubscript{6} single crystal with a large size via hydrothermal method (shown in Figure 2.7).\textsuperscript{119}

![Figure 2.7](image)

Figure 2.7 (a) A schematic diagram of the Cs\textsubscript{2}AgBiBr\textsubscript{6} single crystal grow by hydrothermal reaction process and (b) structure viewed along the [110] direction. (c) High-resolution HAADF-STEM image and (d) the intensity profiles along the [001] direction.\textsuperscript{119}

Luo et al. prepared octahedral shaped crystals of Cs\textsubscript{2}AgInCl\textsubscript{6} with an average size of 2.88 mm × 2.81 mm × 1.95 mm (Figure 2.8a).\textsuperscript{118}

For Tran’s group, they prepare polycrystalline Cs\textsubscript{2}AgSbCl\textsubscript{6} and Cs\textsubscript{2}AgInCl\textsubscript{6} through solid-state reactions first, then the single crystals of Cs\textsubscript{2}AgSbCl\textsubscript{6} and Cs\textsubscript{2}AgInCl\textsubscript{6} were grown hydrothermally by dissolving the polycrystalline Cs\textsubscript{2}AgSbCl\textsubscript{6} (or Cs\textsubscript{2}AgInCl\textsubscript{6}) with 12 M HCl solution in Teflon-lined stainless steel autoclaves, followed by programmed cooling\textsuperscript{120}.

![Figure 2.8](image)

Figure 2.8 The photograph of Cs\textsubscript{2}AgInCl\textsubscript{6} single crystal\textsuperscript{118} (a), Cs\textsubscript{2}AgSbCl\textsubscript{6} single crystal\textsuperscript{120} (b) Cs\textsubscript{2}AgBiCl\textsubscript{6} single crystal (c) and Cs\textsubscript{2}AgBiBr\textsubscript{6} single crystal\textsuperscript{122} (d).
2.2.1.2 Super-saturation crystallization (ambient condition)

There is another facile method to synthesize double perovskite crystal at ambient condition by a saturated solution crystallization strategy.\textsuperscript{11,122,123} Here we use Cs\textsubscript{2}AgBiBr\textsubscript{6} reported by Gao et al. as an example\textsuperscript{11}. 2mmol CsBr and 1mmol BiBr\textsubscript{3} were added in 10 mL of HBr (48\% w/w) and stirred under 110 °C to fully dissolved the solids. Then 1mmol AgBr was added, and the solution was heated to 130 °C. The solution was held at 130 °C for 2 h and then cooled to room temperature. The orange small crystals crystalized from solution upon sitting at room temperature overnight. These small crystals were filtered, washed with methanol twice, and dried under reduced pressure overnight to dry the product.

All the crystals in this thesis were synthesized by this method without temperature control cooling process. So, the crystal size range is much small and varies with different compounds (Figure 2.9).

![Figure 2.9 Crystal sample of Cs\textsubscript{2}AgBiBr\textsubscript{6} (a), Cs\textsubscript{2}NaBiCl\textsubscript{6} (b) and Cs\textsubscript{2}AgInCl\textsubscript{6} (c) synthesized in our work.]

2.2.2 Polycrystalline samples

2.2.2.1 Solution precipitation

McClure et al.\textsuperscript{124} reported a method to prepare polycrystalline Cs\textsubscript{2}AgBiX\textsubscript{6} samples by precipitation from a solution of mixed solvents (hydrohalic acid and hypophosphorous acid). Volonakis et al.\textsuperscript{125} introduced a similar synthesis method for preparing polycrystalline Cs\textsubscript{2}AgInCl\textsubscript{6}. For the acid solution, 10M hydrochloric acid was used, no H\textsubscript{3}PO\textsubscript{2}. This synthesis method is facile and easy to operate. It has been a very universal method to prepare doped and alloyed double perovskite materials.\textsuperscript{12,13,87,126} Most of the double perovskite powder samples in our work were also synthesized by this method, e.g. Figure 2.10.

![Figure 2.10 Polycrystalline sample of Cs\textsubscript{2}AgBiBr\textsubscript{6} (a), Cs\textsubscript{2}AgBiCl\textsubscript{6} (b) and Cs\textsubscript{2}AgInCl\textsubscript{6} (c) synthesized in our work.]

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2.2.2.2 Solid state synthesis

Another widely used method to synthesize polycrystalline double perovskite is solid state reaction. Tran et al. reported polycrystalline Cs$_2$AgSbCl$_6$ and Cs$_2$AgInCl$_6$ synthesized through solid-state reactions under certain vacuum. Filip et al. synthesized Cs$_2$AgBiX$_6$ samples in a silica ampoule that was flame sealed under vacuum ($10^{-3}$ Torr). The mixture was heated to 500°C in 5 hours and held at 500°C for 4 hours. Mcclure et al. prepared polycrystalline Cs$_2$AgBiX$_6$ samples via a different solid state route which is processed at a relatively low temperature in the air. After all the stoichiometric reagents were ground together for 20 min, the mixture powder was loosely placed in an alumina crucible and heated in a box furnace in air at 210 °C for 10 h. At least two heating cycles intermittent re-grindings was needed to obtain nearly phase pure samples. Not surprisingly, the reaction temperature and time of solid-state synthesis varies with different double perovskite compounds. So, multiple attempts and optimization was needed to find the most suitable reaction conditions for synthesizing a new material.

![A photograph of evacuating (a) and sealing (b) the silica glass tube for a solid state synthesis](image)

**Figure 2.11** A photograph of evacuating (a) and sealing (b) the silica glass tube for a solid state synthesis

2.2.2.3 Mechano-synthesis

Mechanosynthesis is a facile, environment friendly and clean solid-state method for preparing various complex materials without the use of solvents. It is an attractive alternative to solvothermal route as it allows shorter reaction times, easy product processing, low reaction energy consumption and no solubility restrictions. Many reports have been published on this synthesis route for hybrid lead perovskite. Recently, several groups introduced this mechanochemical approach to synthesize double perovskites which were not easy to obtained by solvothermal route.
For instance, Kubicki et al. prepared halide mixing double perovskite powders by grinding the reactants in an electric ball mill.$^{138}$

Another case is $\text{Cs}_2\text{AgInBr}_6$, the formation energy reveals it is very challenging to synthesize. $^{82,139,140}$ It is thermodynamically stable but only in a very narrow region of the chemical potential.$^{141}$ Zhao et al. noted that somewhat metastable structures with negative calculated decomposition enthalpy ($\Delta H_{\text{dec}}$) might still be formable since the halide bonds are strong enough to withstand moderate metastability.$^{139}$ Later, Breternitz et al. successfully prepared $\text{Cs}_2\text{AgInBr}_6$ by the mechanochemical approach and revealed that this technique is advantageous for the formation of compounds with narrow existence region.$^{137}$ However, $\text{Cs}_2\text{AgInBr}_6$ degrades very quickly under light illumination. A darkening area could be clearly observed when the compound was exposed to light.

2.2.3 Double perovskite films

The importance of thin film for optoelectronic applications is self-evident. Chemical solution deposition is a facile, low cost and most common method for the fabricating $\text{ABX}_3$ thin films. However, the preparation of high-quality thin films for double perovskites is challenging since the solubilities of most chloride and bromide compounds as the starting materials are
significantly low in most common organic solvents. Instead of directly dissolving binary metal halide precursors, another way was proposed to pre-synthesize crystals first and then redissolve them into the solvent and fabricate films. In fact, the low solubility is still a big issue for most inorganic double perovskite which limits the thin film fabrication with chemical solution deposition. In the thermal evaporation method, the experimental procedure could be relatively simple. In the following section, we will introduce Cs$_2$AgBiX$_6$ thin film fabricated by chemical solution deposition and other double perovskite thin film prepared with thermal evaporation.

![Figure 2.14 Solubility of Cs$_2$AgBiBr$_6$ powder in different organic polar solvents. (the concentration ~0.07 mol/L).]

### 2.2.3.1 Spin coating

Greul et al. and Gao et al. screened several solvents and found dimethylsulfoxide (DMSO) showed the highest ability to dissolve the precursors (CsBr, AgBr, and BiBr$_3$) and the pre-synthesized Cs$_2$AgBiBr$_6$ crystal or powder (Figure 2.14). A typical one-step process for the fabrication of Cs$_2$AgBiBr$_6$ thin films were illustrated in Figure 2.15a. Specifically, all the precursors were completely dissolved in DMSO and form a transparent light yellow solution. Before spin coating, preheat both the solution and substrate at 75°C. Next, the hot solution was spin-coated on the top of the substrate at 2000 rpm for 30 s, followed by annealing at 285°C for 5 min under ambient conditions. Gao et al. indicated that using isopropanol (IPA) as anti-solvent will make the films show yellow mirror-like appearance, and significantly improve the film quality (Figure 2.15b). In addition, compact surfaces and micro-size grains of the film could be achieved when the annealing temperature is greater than 250 °C. DMSO is a solvent with low vapor pressure (0.42 mmHg at 20°C) and high boiling point (189°C) which results in a slow solvent evaporation during spin coating. So, it is not a very ideal solvent for thin film fabrication although it has a certain precursor solubility. Technically, some strategies e.g. hot-casting, low-pressure or solvent engineering will help on address the issue.
Thus, Wu et al. and Lei et al. prepared high quality Cs$_2$AgBiBr$_6$ film by a low-pressure assisted (LPA) method. Zhao et al. and Yang et al. revealed that N,N-dimethylformamide (DMF), with high vapor pressure (2.7 mmHg at 20°C) and low boiling point (153°C) could accelerate the evaporation of DMSO and enlarge the grain size of the film. They used DMSO and DMF mixture as solvent and chlorobenzene (CB) as the antisolvent which fabricated compact Cs$_2$AgBiBr$_6$ thin films with large grain size (Figure 2.15d).

![Schematic of the deposition process for Cs$_2$AgBiBr$_6$ thin films](image)

**Figure 2.15** Schematic of the deposition process for Cs$_2$AgBiBr$_6$ thin films with (a) precursors (dissolved in DMSO), (b) pre-synthesized Cs$_2$AgBiBr$_6$ single crystal powder, (c) precursors (dissolved in DMSO and DMF mixture) and (d) Thin film fabricated by LPA method.

For Cs$_2$AgBiCl$_6$, the solubility is extremely low in all the most common used solvents. Volonakis prepared a dispersion with Cs$_2$BiAgCl$_6$ powder in methyl methacrylate (PMMA) – Toluene solvent. The film was deposited by spin-coating on a glass substrate at 1500 rpm. And the deposition process was repeated several times to obtain uniform thick film. However, thin film materials and devices of Cs$_2$AgBiCl$_6$ and other most double perovskite are still elusive and limited to nanocrystals which restrict further investigation of the optical properties as well as optoelectronic applications. Subsequently, vapor-deposited high-quality double perovskite thin films are going to be introduced.

### 2.2.3.2 Thermal evaporation

There are three main strategies to form perovskite layers through vacuum assisted deposition: single-source evaporation, co-evaporation, and sequential evaporation (Figure 2.16).
Single-source evaporation is a deposition method where only one material source is used (Figure 2.16c). A pre-synthesized perovskite in the form of powders is placed on a metal heater and then, by adjusting the heating current, the material was evaporated and transferred onto the substrate maintaining the initial stoichiometry and composition.\textsuperscript{152,153}

For co-evaporation process, starting materials are loaded in two or more separate crucibles which are then heated in a high vacuum chamber until they begin to evaporate and deposit on the substrate. Sequential method is similar with co-evaporation process except that the precursors are evaporated one by one, and more layers could be deposited to obtain a thick film. Thus, the as-deposited film is usually annealed to ensure complete conversion of the precursors to perovskite. For these two methods, the stoichiometry of the constituent in the final film can be finely tuned by the control of the evaporation rates of each single component. The material volume ratio, depending on the molecular weight and densities, is proportional to the film thickness. Thus, the volume ratio is equal to the deposition rate ratio. Accordingly, López-Fraguas et al. calculated deposition rate for fabricating CsSnI\textsubscript{3} as below\textsuperscript{154}:

\[
\frac{1\text{mol CsI}}{1\text{mol SnI}_2} \rightarrow \frac{259.81 \text{ g CsI}}{372.52 \text{ g SnI}_2} \rightarrow \frac{57.61 \text{ mL CsI}}{49 \text{ mL SnI}_2} = \frac{\text{deposition rate CsI}}{\text{deposition rate SnI}_2} = 1.176 \quad (2.1)
\]

Wang et al. prepared Cs\textsubscript{2}AgBiCl\textsubscript{6} by sequential vapor deposition with evaporator under pressure below 1.0 x 10\textsuperscript{-3} Pa. CsCl, BiCl\textsubscript{3}, and AgCl are deposited on the substrates layer by layer sequentially. According to the calculated thickness ratio, each deposition cycle parameter was set as “CsCl-98 nm, BiCl\textsubscript{3}-77 nm, AgCl-30 nm” and a thick film could be attained when the deposition cycle was simply repeated\textsuperscript{94}. Luo et al. reported Bi doped Cs\textsubscript{2}Ag\textsubscript{0.60}Na\textsubscript{0.40}InCl\textsubscript{6} film deposited by thermal evaporation under pressure 6 x 10\textsuperscript{-6} mTorr. Stoichiometric molar ratio of the precursors, CsCl, AgCl, NaCl, InCl\textsubscript{3} and BiCl\textsubscript{3}, was 2:0.6:0.4:1:~0.005.\textsuperscript{23} Wang et al. revealed that excess BiBr\textsubscript{3} is helpful to eliminate the impurity phases in the films when they fabricated Cs\textsubscript{2}AgBiBr\textsubscript{6} films with sequential vapor deposition. High quality films were obtained with optimized molar ratio of BiBr\textsubscript{3}: AgBr: CsBr as 1.5:1:2 instead of the theoretical one( 1:1:2)\textsuperscript{155}. Thus, for sequential vapor deposition, the fabrication is complicated since the composition ratios of the final formed Cs\textsubscript{2}AgBiBr\textsubscript{6} films may greatly deviated from the ideal stoichiometry. Fan et al. demonstrated the Cs\textsubscript{2}AgBiBr\textsubscript{6} thin films that were prepared with single source vapor deposition. First, Cs\textsubscript{2}AgBiBr\textsubscript{6} crystal was synthesized and then grinded into powder. Next, the powder sample was placed in tungsten boat and
evaporated with programmed heating, adjusting the heating current from 0 A to 120 A at a rate of 20 A/min.\textsuperscript{153}

![Figure 2.16 Scheme of (a) co-evaporation fabrication process of CsSnI\textsubscript{3},\textsuperscript{154} (b) sequential vapor deposition process of CsAgBiBr\textsubscript{6} thin film\textsuperscript{155} and (c) single-source evaporation deposition process of CsAgBiBr\textsubscript{6} thin film\textsuperscript{153}](image)

Considering the low solubility of both double perovskite and their precursors in common solvents, thermal evaporation seems the most desirable method to prepare high-quality films for devices in commercial applications.

### 2.2.4 Nanocrystal

As mentioned above, the solubility of double perovskite is an issue which limits the preparation of high-quality film, thus, number of works reported the study of nanocrystal for double perovskite materials.\textsuperscript{156–159} Here, Cs\textsubscript{2}AgInCl\textsubscript{6} is used as an example to introduce the hot-injection approach which is the most common method to prepare nanocrystal as illustrated in Figure 2.17. Firstly, concentration of 0.5 M cesium-oleate is prepared by mixing cesium carbonate (Cs\textsubscript{2}CO\textsubscript{3}) with oleic acid (OAc) under inert atmosphere. The product is collected and stored in a vial under air. Then 1:1 mol ratio of silver acetate (Ag(OAc)), indium acetate (In(OAc)\textsubscript{3}) are mixed with oleylamine (OAm), cesium-oleate solution and diphenyl ether (DPE) in a three-neck flask and dried under vacuum. Then temperature is programmed increased to 105 °C under nitrogen atmosphere, upon reaching this temperature, mixtures of degassed benzoyl chloride (Bz-Cl) and DPE was swiftly injected into the flask. After 5s, the solution is cooled down with an ice–water bath. The NCs products were separated by centrifugation.\textsuperscript{156}

Another simpler method was introduced without preparing cesium-oleate solution.\textsuperscript{157} Specifically, directly add Cs\textsubscript{2}CO\textsubscript{3}, Ag(OAc), (In(OAc)\textsubscript{3}) to mixture of 1-octadecene (ODE), oleic acid (OA), and OAm and then degass under vacuum for 2 h at 100 °C. The solution was then
heated to 200 °C under N₂ atmosphere. Subsequently, when the temperature arrives, chlorotrimethylsilane (TMS-Cl) in ODE is swiftly injected. Then follows cooled down step with ice-water bath and product collection with centrifugation.

![Schematic diagram of nanocrystals (NCs) with “hot-injection” synthesis approach (Deutsches Elektronen-Synchrotron DESY)](image)

**Figure 2.17** Schematic diagram of nanocrystals (NCs) with “hot-injection” synthesis approach (Deutsches Elektronen-Synchrotron DESY)

### 2.3 Characterization of double perovskite

#### 2.3.1 X-ray diffraction

X-ray diffraction (XRD) is a well-known powerful analysis method to study the crystalline structure of materials since typical interatomic distances in a solid are on the order of an angstrom¹⁶⁰ (0.1nm) which are comparable to X-ray wavelengths (ranging from 0.01 to 10 nm). This technique can measure the average spacing of planes in a crystal lattice and provide information on unit cell dimensions. It involves a fundamental principle, namely Bragg's law.

**2.3.1.1 X-ray Radiation Source**

X-Rays are produced in an X-Ray Tube (Figure 2.18). The tube consists of an evacuated chamber with a cathode (a metal filament) and an anode (a metal plate) on its ends. A current flow through the filament which then emits electrons because of thermionic effect, these electrons are accelerated towards the anode (target) by a large voltage difference (30-150 kV). The electrons bombarding the target metal plate and ionize the inner shells electrons of the target atoms, subsequently, the electrons from outer shells relax to lower energy levels through radiative emission of X-rays.¹⁶¹
Transitions from the L to K shell produce the typical Kα X-Ray while transitions from M to K shell produce the Kβ line. The Kβ are usually less intense than the Kα and are filtered by a monochromator. The Kα X-Ray are further divided into Kα1 (transition from L\(_3\) (2p\(_{3/2}\) \(\rightarrow\) K(1s)) and Kα2 (transition from L\(_2\) (2p\(_{1/2}\) \(\rightarrow\) K(1s)). Here the instrument used is Bruker D8 Advance, has a target made of copper (Cu) and the radiation wavelengths of Cu Kα1 and Cu Kα2 are 1.540598 Å and 1.544426 Å, respectively.

![Figure 2.18 Schematic view of (a) conventional x-ray tube and (b) Copper characteristic X rays](image)

### 2.3.1.2 Bragg’s law

Consider a crystal in which atoms and molecules has a periodic arrangement (Figure 2.19), we assume A–A’ and B–B’ are two parallel planes of atoms with same Miller indices (hkl) and separated by an interplanar distance of \(d_{hk\ell}\). When a parallel, monochromatic X-Rays is incident on these two planes at an angle \(\theta\), the two X-Rays (1 and 2) are scattered by atoms P and Q and the scattered rays (1’ and 2’) occurs also at an angle \(\theta\) to the planes. But there is a path length difference (2\(\cdot\)d\(\cdot\)sin\(\theta\)) between scattered ray 1’ and 2’ because of path SQ and QT in beam 2 and 2’. Diffraction peaks will be generated only when the waves that are in phase interfere constructively, which means the path length difference is an integral number of wavelengths (n\(\cdot\)λ). This observation leads to Bragg’s law:

\[
n\lambda = 2d_{hk\ell}\sin\theta \tag{2.2}
\]

Since we know the radiation wavelength \(\lambda\), with the measured angles \(\theta\) at which constructive interference occurs we can know the interplanar distance:

\[
d_{hk\ell} = \frac{n\lambda}{2\sin\theta} \tag{2.3}
\]
Furthermore, the lattice parameter \( a \) could be calculated from interplanar distance \( d_{hkl} \) and Miller indices \((h, k, l)\), e.g. for crystal structures with cubic symmetry:

\[
d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}
\]  

(2.4)

2.3.1.3 Bragg-Brentano geometry

The Bragg-Brentano diffractometer is the dominant geometry found in most laboratories. If the tube is fixed, the sample and detector are rotated by \( \theta \) and \( 2\theta \) respectively, this is called \( \theta-2\theta \) geometry as shown in the schematic of Figure 2.20b. In this type of diffractometer, sample surface is kept on the tangent plane of the focusing circle defined by three spots at sample, X-ray source and receiving slit. The incident-beam slit and diffracted-beam slit move on a circle that is centered on the sample (goniometer circle). Divergent X rays from the source hit the sample at different points on its surface. During the diffraction process the X rays are refocused at the detector slit. The diffraction peak position is recorded as the detector angle, \( 2\theta \).

Figure 2.20 (a) Bruker D8 ADVANCE diffractometer. (b) Schematic of a diffractometer with a Bragg-Brentano geometry.
High-resolution XRD measurements in this work were performed using standard Bragg Brentano configuration. This type of arrangement was provided using Bruker D8 ADVANCE diffractometer with $\theta - 2\theta$ geometry and Cu Kα radiation, and the acquisition is done for every 0.04° increment over the Bragg angle range of $2\theta = 10° - 65°$. Before characterizations, a polycrystalline sample or a crystal sample should be ground into a fine powder in a mortar and then mounted on a plate.

2.3.1.4 Rietveld Refinement and Phase Analysis

Once PXRD diffraction patterns is collected, they are initially compared with reflections corresponding to the expected structure. For the reflection peaks unaccounted for, check the phase of initial reagents and further expand to simple binary, ternary, or quaternary phases that could reasonably occur, including oxygen containing and hydrated phases. Crystallographic Information Files (CIF) were used as the starting point for refinements.\(^{163}\) Rietveld method is a technique in which the diffraction profile of a powder is simulated point by point knowing the crystal structure and instrumental and microstructural information.\(^{164}\) Using all these parameters the diffraction profile can be computed and compared to the experimental one, here the software used is MAUD.\(^{165}\) Some crystal data could be extracted from the refinement. For an impure composition, it also can analyze the phase percentages.

![Rietveld analysis of Cs$_2$AgInCl$_6$ using MAUD. The black diamond points show the experimental data, the red line represent the fitted simulated profile, the difference of them is shown below the main plot, black vertical bars indicate the angular positions of the allowed Bragg reflections. $R_{wp}$ (%) = 9.53, and $GOF = 1.50$](image)

Figure 2.21 Rietveld analysis of Cs$_2$AgInCl$_6$ using MAUD. The black diamond points show the experimental data, the red line represent the fitted simulated profile, the difference of them is shown below the main plot, black vertical bars indicate the angular positions of the allowed Bragg reflections. $R_{wp}$ (%) = 9.53, and $GOF = 1.50$
2.3.2 Inductively coupled plasma optical emission spectrometer (ICP-OES)

ICP-OES is an analytical technique which could be used for the detection of chemical elements.

Specifically, the solution to be analysed is conducted by a peristaltic pump though a nebulizer into a spray chamber. Then the produced aerosol is introduced into an argon plasma which excite electrons to higher energy level due to thermic energy. Upon relaxation of these electrons to ground state, energy is emitted in the form of photons. The wavelengths of emitted photons are measured with a spectrometer and each element features characteristic emission spectrum. The light intensity on the wavelength could be measured and calculated into a concentration with the calibration. In this work, ICP-OES measurements were carried out using Agilent 5110.

![Schematic diagram of ICP-OES](image)

Figure 2.22 Schematic diagram of ICP-OES (AQA Scientific).

2.3.3 Absolute PL quantum yield and fluorescence lifetime

2.3.3.1 Photoluminescence quantum yield (PLQY) measurement

For the light-emitting materials, it is essential for measuring the PLQY, which is defined as the ratio of the number of emitted photons ($P_{N_{em}}$) to the number of absorbed photons ($P_{N_{abs}}$) and expressed by the following equation.

$$\phi = \frac{P_{N_{em}}}{P_{N_{abs}}}$$ (2.5)

In this work, PLQY of the sample powders were all measured on an absolute PLQY spectrometer (Quantaurus-QY C11347, Hamamatsu). For the excitation light source, it consists of a xenon lamp, a monochromator and an integrating sphere which is coated with highly reflective material. The multiple excitation wavelengths are controlled automatically.
during the measurements, and except for PLQY measurement, there are more selection of analysis functions, including PL spectrum and PL excitation spectrum.\textsuperscript{166}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{(a) Principle of quantum yield measurement and Quantaurus-QY measured (b) PL spectrum of Cs\textsubscript{2}Na\textsubscript{1-x}Ag\textsubscript{x}In\textsubscript{0.99}Bi\textsubscript{0.01}Cl\textsubscript{6}. (c) PLE/PL mapping of Cs\textsubscript{2}Na\textsubscript{0.6}Ag\textsubscript{0.4}In\textsubscript{0.99}Bi\textsubscript{0.01}Cl\textsubscript{6}.}
\end{figure}

2.3.3.2 Fluorescence lifetime measurement

Fluorescence is the spontaneous emission of radiation from excited states, with relaxation to a low-energy state in the same spin multiplicity as the emitting excited state. If spin multiplicity is different between the initial and final states, the phenomenon is called phosphorescence.

When substances are excited by absorption of a radiation from the ground state to excited state, the electron returns to ground state via several relaxation pathways which are classified into radiative process and non-radiative process. The radiative and non-radiative process compete with each other. Quantum yield of fluorescence, $\phi$, and the fluorescence decay time, $\tau$ (tau), are the important photophysical parameters for a steady state absorption-emission system, which are defined by equations:

\begin{align}
\phi &= \frac{k_f}{(k_f + k_{iSC} + k_{iC} + k_d)} \\
\tau &= \left(\frac{1}{k_f + k_{iSC} + k_{iC} + k_d}\right)^{-1}
\end{align}

\textsuperscript{2.6} \textsuperscript{2.7}
Where \( k_f \) is the radiative rate constant, \( k_{ISC} \) is the rate constant of intersystem crossing, \( k_{IC} \) is the rate constant of radiationless internal conversion and \( k_d \) is the rate constant of formation of products.\(^{167}\)

Thus, there is a close relationship between \( \tau \) and \( \phi \) as shown in the following equation, and these parameters are fundamental and very important in controlling the emission properties of luminescent materials.

\[
k_f = \frac{\phi}{\tau}
\]  

(2.8)

Figure 2.24 shows Fluorescence lifetime of Cs\(_2\)AgInCl\(_6\) and Cs\(_2\)AgIn\(_{0.99}\)Bi\(_{0.01}\)Cl\(_6\) measured by Quantaurus-Tau with excitation wavelength at 280nm and time range of 1\(\mu\)s.

![Figure 2.24 Fluorescence lifetime of Cs\(_2\)AgInCl\(_6\) and Cs\(_2\)AgIn\(_{0.99}\)Bi\(_{0.01}\)Cl\(_6\) (excitation wavelength at 280nm)](image)

2.3.4 Ultraviolet-visible light (UV-vis) Spectroscopy

2.3.4.1 Absorptance (A), absorbance (A\(_{abs}\)) and absorption coefficient (\(\alpha\))

When the light is incident on the sample, it will be partially reflected, transmitted, and absorbed (Figure 2.25). By measuring the reflectance, \((R = \frac{I_R}{I_i})\) and transmittance, \((T = \frac{I_T}{I_i})\), we can obtain the fraction that is absorbed (i.e. absorptance), \(A\), which is given by,

\[
A = 1 - R - T
\]  

(2.9)

![Figure 2.25 A schematic diagram showing how thermal radiation interacts with a surface through reflection, transmission, and absorption.](image)
According to Beer–Lambert law, when a light beam of intensity $I$, illuminating on the sample cell, a fraction of the light $\alpha \times dx$ entering the cell of thickness $dx$ will be absorbed,

$$\frac{dI}{I} = -\alpha dx$$ \hspace{1cm} (2.10)

Integrating equation (2.10) for uniform $\alpha$ at a depth $x$, the light intensity will be attenuated by a factor of $\exp[-\alpha \times dx]^{168}$,

$$I_x = I_0 e^{-\alpha x}$$ \hspace{1cm} (2.11)

where $I_0$ is the intensity of the light transmitted through the sample.

Consider the path length of the light through the material is $d$ (e.g. the thickness of a film), substituting equation (2.9) into equation (2.11),

$$I_T = I_0 e^{-\alpha x} = [I_\lambda - I_R] e^{-\alpha d}$$ \hspace{1cm} (2.12)

Often, we use the term absorbance, $A$ (this is different from absorptance), which refers to attenuation of light through a material and is defined as,

$$A = -\log_{10} \left[ \frac{I_T}{I_0} \right]$$ \hspace{1cm} (2.13)

As can be seen from equation (2.12) and (2.13), the absorption coefficient $\alpha$ can be expressed as,

$$\alpha (cm^{-1}) = \frac{A}{d(cm)} \times \ln(10)$$ \hspace{1cm} (2.14)

2.3.4.2 Diffuse Reflectance measurements

Reflection consists of two components: specular reflection and diffuse reflection. Specular reflection occurs when incident light is reflected symmetrically with respect to the normal line, while diffuse reflectance occurs when incident light is scattered at various angles. Specularly reflected light is not involved in an absorption process, and therefore contains almost no information about the electronic states within the material while diffuse reflected light penetrates the sample surface, is partially absorbed, and a fraction of which is reemitted (reflected) at various nonincident angles as depicted in Figure 2.26a.\textsuperscript{169}

A typical configuration for a diffuse reflectance measurement involves the use of an integrating sphere which can capture all photons that are reflected in all directions from the sample.\textsuperscript{169} Powder or film samples are best suitable to this configuration. Figure 6b shows a double beam integrating sphere spectrometer. With a rotating mirror, the light beam is split in reference and sample beams which alternately enter the integrating sphere through the
two ports. The detector alternately measures light that was reflected from the sample, \( I_R \), or a standard, \( I_t \), and then the instrument ratios the two signals which obtain the reflectance, \( R \).

![Diagram of diffuse reflection on sample](image1)

**Figure 2.26** (a) Schematic diagram of diffuse reflection on sample. (b) Double beam reflectance spectrometer with integrating sphere.\(^{170}\)

However, during the diffuse reflectance measurements, specular reflection will increase noise, decrease the accuracy of the measurement, and even contribute to spurious peaks in the data.

For powders, dilution in a nonabsorbing matrix materials such as KBr, KCl, and Ba\(_2\)SO\(_4\) can further increase diffuse reflectance while minimizing specular reflectance.\(^{169}\)

### 2.3.4.3 Analysis of band gap with Tauc plot

The optical band gap energy (\( E_g \)) of a semiconductor material could be calculated following Tauc law relation:\(^{171,172}\)

\[
\alpha h\nu \propto (h\nu - E_g)^{1/n}
\]

(2.15)

where the assignment to \( n \) the values of 1/2 for direct transition and 2 for indirect transition, \( \alpha \) is absorption coefficient. Often the value \( \alpha > 10^4 \text{ cm}^{-1} \) obeys well the relation while for values of \( \alpha < 10^4 \text{ cm}^{-1} \), an exponential tail exists for many materials, and fitting a tangent to a point within this tail will underestimate the band gap of the material as can be observed in Figure 2.27.\(^{169}\)
Figure 2.27 Tauc plot of direct band gap (solid black) and absorption coefficient plot (solid red) of MoS$_2$. Extrapolation of $(\alpha h\nu)^2$ to the baseline by using a range of $\alpha > 4.5 \times 10^4$ cm$^{-1}$ (dashed black) obtain the band gap while fitting the low energy exponential tail region may result in an underestimate of the band gap (dashed blue and dashed orange).\textsuperscript{170}

In the case of a diffuse reflectance measurement, in which the Kubelka–Munk function can be employed to extract $\alpha$ and given by,\textsuperscript{173}

$$F(R) = \frac{(1-R)^2}{2R} = \frac{\alpha}{s}$$

(2.16)

where $F(R)$ denotes the Kubelka–Munk function, $R$ denotes diffuse reflectance and $s$ denotes the scattering coefficient. If the scattering coefficient is assumed to be wavelength independent, the Tauc law relation was adapted adequately by the substitution of $\alpha$ with $F(R)$. Plotting $(F(R)h\nu)^{1/n}$ against $h\nu$ and extrapolating the curve to the $x$-intercept is used for determining $E_g$ values.\textsuperscript{163,174,175} It must be taken care to extrapolate the band gap from higher values of $F(R)$ to avoid the underestimation in exponential tail region as discussed above since the accurate value of $\alpha$ is not possible to plot without knowing the scattering coefficient.\textsuperscript{170}

Figure 2.28 (a) Absorbance data, (b) Normalized absorption coefficient vs. energy and (c) Allowed direct band gap Tauc plots from a film of electrodeposited polycrystalline Cu$_2$O.\textsuperscript{169}
Furthermore, note that it could lead error for the assumption of wavelength independency for $s$ since the transformed data, $F(R)$, is not linearly proportional to the absorption coefficient in many situations. Murphy described a more rigorous analysis to obtain the absorption coefficient from diffuse reflectance.$^{176,177}$

In the case of this thesis, diffused transmission and reflection were measured by Agilent Technologies Cary 5000 UV−vis−NIR to obtain UV−vis optical absorption of double perovskite powders and the band gap of which with Tauc plots.

### 2.3.5 Ultrafast spectroscopy techniques

There are typically two ultrafast spectroscopy techniques to study the optical properties of perovskites, i.e. time resolved photoluminescence (TRPL) and differential transmission (DT), also known as transient absorption or pump-probe.

#### 2.3.5.1 Transient absorption spectroscopy

Ultrafast transient absorption spectroscopy (TAS) is a pump-probe spectroscopic technique utilized to measure the photogenerated excited state absorption energies and associated lifetimes of molecules, materials, and devices. It provides information not only on the excited states of the system but also on all the intermediate evolutionary transients and non-emissive states both on the ground and the excited states. The pump-probe measurement setup consists of laser source, optical parametric amplifier (OPA) and ultrafast spectrometer.

The core of the experimental setup is represented by the light source, here an ultrafast laser used was a Ti: sapphire regenerative amplifier (Coherent Libra) that produce pulses of less than 100 fs duration, 794 nm in wavelength, with energies larger than 1 mJ at a 1 kHz repetition rate.$^{178}$ Then to pump our samples with a single photon process, the beam’s wavelength should be tuned so that the photon energy would be larger than the band gap of the samples. This could be achieved by optical parametric amplifier (OPA).$^{179}$

#### 2.3.5.1.1 Measurement of pump-probe

As illustrated in Figure 2.29, in pump-probe system, the laser pulse is split to two pulses by a beam splitter which are called pump pulse and probe pulse. Then the sample is photo-excited by pump pulse, herein, using a delay line, probe pulse is measured for transient perturbation changes in absorption as a function of wavelength and time. In fact, the absorption could not be measured directly, the detector time-integrates the signal transmitted, by measuring the
differential transmission (DT) with different delay time, the dynamic process of the samples could be studied. In this work, the $\Delta T/T$ is measured. Normally, the intensity of pump pulse is much higher than the probe pulse and pump pulse also has a larger size of beam spot that can totally overlap probe beam spot. For the probe, it is very useful to use a supercontinuum white, in order to obtain the DT along all the visible spectrums. The transmittance of the sample in the ground state $T_0$ can be measured by blocking one out of two pump pulses with a chopper.\textsuperscript{179}

![Figure 2.29 The schematic diagram of setup used for the pump-probe measurement.\textsuperscript{179}](image)

2.3.5.1.2 Principle of pump-probe

If there is no pump pulse work on the sample, the sample in the ground state will absorb the incident probe pulse. However, after the pump pulse strike on the sample, electrons were excited to the conduction band, and the population of electrons in the valence band decreased. Therefore, the sample absorption decreases, and the DT increases. For this phenomenon, a peak could be observed in the $\Delta T/T$ plot just after the pump strikes the sample which is called photobleaching. Furthermore, it is also possible to appear another two phenomena. The probe can create a stimulated emission in the sample and increases the differential transmission. Or the absorption of the probe pulse leads to excitation of electrons from an excited state to another higher excited state. In this case, the DT is negative since this transition was not available before the excitation.

2.3.5.2 Time-resolved photoluminescence (TRPL)

TRPL is measured by exciting luminescence from a sample with a short laser pulse on time scales of pico to nano second, and then a fast detector is used to observe decay in photoluminescence (PL) as a function of time. This technique can be used to measure optical
property of materials such as the emission lifetime, or it helps to study energy transfer from one component to another in mixed systems. The duration of pulses on the nanosecond timescale are slow enough to be measured through electronic means. In a streak camera, the emitted light passes through a slit and strikes to a photocathode, in which photons are “converted” into electrons. In addition, the number of electrons is proportional to the number of photons. And the electrons are then accelerated passing through a pair of accelerating electrodes and bombarded against a phosphor screen. The dynamics of optical gain in the materials could be studied through a streak camera.

2.3.5.3 Tandem spectroscopy ultrafast

For TRPL, it collects the luminescence of the material under pulsed laser excitation, so it is only sensitive to radiative species. On the other hand, time evolution of DT can monitor all optical excitations, even if they cannot emit light (“dark states”). Furthermore, DT signal is directly proportional to the excited-state population density, while the PL signal follows a power law with an exponent equal to the order of the recombination process leading to the emission: it is directly proportional to population density for monomolecular recombination, while proportional to the square of the population for bimolecular recombination. Another problem is that, the intrinsic property may vary from area to area on a sample. Moreover, DT and PL setups is also not easy to ensure employing the totally same excitation laser pulses. To solve these issues, a tandem spectroscopy technique that combines photoluminescence and differential transmission is applied.

Figure 2.30. The schematic diagram of ultrafast tandem spectroscopy setup.\textsuperscript{178}
In this work, crystals were prepared to do the tandem spectroscopy measurements. The crystals with suitable size were left on a piece of clean glass, then dropped ethanol on the crystals. After the ethanol evaporated, the crystals would stick on the glass (Figure 2.31a). And as observed from Figure 2.31b, the laser spotted at the center of the crystal which avoids the excitation on the crystal edge.

Figure 2.31 (a), Crystals were prepared on the glass for the measurement of tandem spectroscopy. (b) Photos of laser spot on the crystal.
In this chapter, firstly, double perovskite materials Cs$_2$AgInCl$_6$, Cs$_2$NaInCl$_6$, Cs$_2$AgBiCl$_6$, and Cs$_2$NaBiCl$_6$ were successfully synthesized. They all have highly symmetric face-centered cubic structures (space group belong to Fm$ar{3}$m), consisting of a 3D framework of corner connected octahedra $[B^+\text{Cl}_6]^{3-}$ or $[B^{3+}\text{Cl}_6]^{5-}$ ($B^{3+}$=Bi$^{3+}$ or In$^{3+}$; $B^+$=Ag$^+$, Na$^+$ or Cu$^+$), with Cs$^+$ ions occupying the octahedral external cavities in the framework. Cs$_2$AgInCl$_6$ and Cs$_2$NaInCl$_6$ have direct band gaps but the dipole transitions between the band edge states are parity-forbidden which leads to relatively large optical band gaps (3.5ev and 5.1 eV respectively). Notably, Cs$_2$AgInCl$_6$ showed both a sharp UV emission and a broad emission which a trade-off relation as the temperature is changing which can be explained by de-trapping. For Cs$_2$AgInCl$_6$, after excitation, holes were quickly trapped at $[\text{AgCl}_6]$ octahedra and change the electronic configuration of silver from 4$d^{10}$ to 4$d^9$ which induce a strong Jahn–Teller distortion of $[\text{AgCl}_6]$ octahedron, giving rise to a broadband emission centered at $\sim$600nm at low temperature. However, compared with the much-localized hole wave function, the electron wave function was rather spread, leading to the small overlap between hole wave function and electron wave function. Thus, the dark transition of free excitons and self-trapped excitons (STEs) results in extremely low radiative recombination rates (PLQY $<$0.1%). Remarkably, the emission efficiency was enhanced when Na was alloyed, since the STEs were confined by the surrounding $[\text{NaCl}_6]^{5-}$ octahedra barrier, thus enhancing the electron and hole orbital overlap and increasing the transition dipole moment. The addition of a small fraction of Bi in Cs$_2$Na$_{1-x}$Ag$_x$InCl$_6$, namely 1%, tremendously improve the emission properties. The PLQY could be closed to unity when Ag content range from 0.2 to 0.4 while the emission spectrum doesn’t change. The comparison of tandem spectroscopy on materials Cs$_2$Na$_{0.6}$Ag$_{0.4}$InCl$_6$ without Bi and with 1% Bi, reveals that the transient absorption (TA) decay time is much longer than the PL lifetime for the sample without bismuth which can be explained by the presence of defects like traps that make the emission not efficient. But for the Bi doped samples, the pump-probe decay time is comparable to the PL lifetime which is compatible with the fact that optical excitations are captured by the presence of new states above the valence band maximum (VBM) which was created by Bi, instead of being trapped by defects, so the recombination is totally radiative.

Cs$_2$AgBiCl$_6$ and Cs$_2$NaBiCl$_6$ both possess indirect band gap. By introducing trivalent In$^{3+}$, the In/Bi alloyed double perovskites could tune the convergence of direct and indirect bandgaps by varying the ratio between In and Bi. Interestingly, Cs$_2$NaIn$_{1-y}$Bi$_{y}$Cl$_6$ materials have no emission, but the addition of 1% of Ag increases dramatically the emission in the visible range. All the measurements confirmed that the white emission is produced by STEs derived from large electron–phonon coupling and soft lattice in the double perovskite compounds, but the outstanding emission properties are due to the simultaneous presence of Bi and Ag. The exact mechanism for this high efficiency is still under investigation and up to now it is well known that the optical properties are highly related to the synthesis techniques because they affect the surface traps and defects. Thus, in the last part of the chapter, I will also display the differences of optical performance between powder and crystal, and it is assumed that it is due to the different microstructure in lattice (e.g. defects and disorder). (It should be noted that for element ratios in the alloyed compositions below, the description for crystal structure analysis round to two decimal places while the compounds writing in TRPL measures round to one decimal place.)
3.1 Experiments

**Chemicals:** Caesium chloride (CsCl, 99.999%), silver nitrate (AgNO₃, 99.9%), Indium chloride (InCl₃, 99.999%), indium oxide (In₂O₃, 99.95%), and hydrochloric acid (HCl, 36%) were purchased from Alfa Aesar. Sodium chloride (NaCl, >99%), bismuth oxide (Bi₂O₃, 99.9%) and bismuth chloride (BiCl₃, 99.9%) were purchased from Sigma Aldrich. Potassium chloride (KCl, >99.5%) was purchased from Merck & Co. AgCl was precipitated from as prepared aqueous solutions of AgNO₃ and KCl.

**Synthesis of Cs₂AgInCl₆ powder:** The synthesis of Cs₂AgInCl₆ powder was prepared by precipitation from an acid solution following the procedure described in reference 125. 1 mmol of InCl₃ was first dissolved in 5 mL 10 M HCl at room temperature, then AgCl was added. After several minutes, 2 mmol of CsCl was added and the solution is heated to 115 °C. Immediately after the addition of CsCl, a white precipitate forms and the hot solution was held at 115 °C for 30 min to ensure a complete reaction. The solid precipitate is then filtered and washed with ethanol before drying it at low pressure. The yield of the obtained product is around 78%.

![Scheme of the synthesis method of Cs₂AgInCl₆ powder](image)

**Synthesis of Cs₂AgInCl₆ crystal:** As mentioned in the last part of Chapter 2, tandem spectroscopy that combines Time-resolved photoluminescence and differential transmission could be a good method to learn time evolution of all optical excitations. However, for this measurement, powder is not suitable because of scattering issue while thin films and single crystal is more appropriate. Whereas, thin film of double perovskite is not easy to be prepared with spin coating since there is no organic solvent could have the double perovskite dissolved well. So here, some small crystals with size of few hundreds of micrometers were prepared.
with supersaturated solution for measuring tandem spectroscopy. And as shown in Figure 2.31b, the size of these small crystal is enough to ensure the measurements.

Different from synthesizing Cs$_2$AgInCl$_6$ powder, the synthesis of Cs$_2$AgInCl$_6$ crystal is similar with the synthesis process of Cs$_2$AgBiBr$_6$ crystal$^{11}$. Here the HCl was used with higher concentration of 12M, and the most important thing is to have supersaturated solution. Specifically, 0.5 mmol In$_2$O$_3$ was added in 10 mL 12M HCl solution and stirred under 110°C to be fully dissolved. 2 mmol of CsCl was added and white precipitate formed immediately. Keep on adding HCl until the solution turned to be transparent. Then 1 mmol of AgCl were added and white precipitate formed again. The solution was heated to be 120°C. Added more HCl to make the solution just turned to be transparent. And the solution was held at 120°C for 2 h. The stir bar was removed from the solution before the solution was cooled to room temperature. Some small crystals with size of 50-500 μm formed from solution upon sitting at room temperature overnight. These crystals were filtered with buchner funnel, washed with ethanol, and dried under reduced pressure overnight. The yield of the obtained product is around 75%. For small crystals of Cs$_2$AgBiCl$_6$, Cs$_2$NaBiCl$_6$, Cs$_2$NaInCl$_6$, they were prepared by the same synthesis method.

**Synthesis of alloyed Cs$_2$Na$_{1-x}$Ag$_x$InCl$_6$ double perovskite small crystals:** Small single crystals of alloyed double perovskite were all crystallized following the synthesis method of Cs$_2$AgInCl$_6$ crystal. Briefly, for preparing 1mmol Cs$_2$Na$_{1-x}$Ag$_x$InCl$_6$, 0.5 mmol In$_2$O$_3$ was added in 10 mL HCl solution and stirred under 110°C be fully dissolved. 2 mmol of CsCl was then added and white precipitate formed immediately. Keep on adding HCl until the solution turned to be transparent. Then $x$ mmol of AgCl and 1–$x$ mmol of NaCl were added and white precipitate formed again. The solution started to be heated to 120°C. More HCl could be added to make the solution just turned to be transparent. The solution was held at 120°C for 2 h. The stir bar
was removed from the solution before the solution was cooled to room temperature. Some small crystals with size of 50-500 μm formed from solution upon sitting at room temperature overnight. These crystals were filtered with buchner funnel, washed with ethanol, and dried under reduced pressure overnight. The yield of the obtained product is about 75%. Bi-doped alloyed double perovskite was synthesized by substituting the In₂O₃ with a mixture of 0.495 mmol In₂O₃ and 0.005 mmol Bi₂O₃ in 10 mL HCl solution, and then followed the same procedure as for the Cs₂Na₁₋ₓAgₓInCl₆ synthesis.

**Synthesis of alloyed Cs₂NaBi₁₋ₓInₓCl₆ double perovskite small crystals:** A mixture of 0.5x mmol In₂O₃ and 0.5x(1-x) mmol Bi₂O₃ was added in 10 mL HCl solution and stirred under 110°C to be fully dissolved. 2 mmol of CsCl was then added and white precipitate formed immediately. Keep on adding HCl until the solution turned to be transparent. Then 1 mmol NaCl were added, and the solution started to be heated to 120°C. More HCl could be added to make the solution just turned to be transparent. The solution was held at 120°C for 2 h. The stir bar was removed from the solution before the solution was cooled to room temperature. Some small crystals with size from 100 μm to 1cm formed from solution upon sitting at room temperature overnight. These crystals were filtered with buchner funnel, washed with ethanol, and dried under reduced pressure overnight. Ag-doped alloyed double perovskite was synthesized by substituting the NaCl with a mixture of 0.99 mmol NaCl and 0.01 mmol AgCl, and then followed the same procedure as for the Cs₂NaBi₁₋ₓInₓCl₆ synthesis.

**Synthesis of alloyed Cs₂AgBi₁₋ₓInₓCl₆ double perovskite small crystals:** A mixture of 0.5x mmol In₂O₃ and 0.5x(1-x) mmol Bi₂O₃ was added in 10 mL HCl solution and stirred under 110°C to be fully dissolved. 2 mmol of CsCl was then added and white precipitate formed immediately. Keep on adding HCl until the solution turned to be transparent. Then 1 mmol AgCl were added and the solution started to be heated to 120°C. More HCl could be added to make the solution just turned to be transparent. The solution was held at 120°C for 2 h. The stir bar was removed from the solution before the solution was cooled to room temperature. Some small crystals with size of 50-500 μm formed from solution upon sitting at room temperature overnight. These crystals were filtered with buchner funnel, washed with ethanol, and dried under reduced pressure overnight.

**Synthesis of powders for alloyed Cs₂Na₁₋ₓAgₓInCl₆ double perovskite:** Here, I also prepared powders for alloyed double perovskite Cs₂Na₁₋ₓAgₓInCl₆ following the synthesis method preparing Cs₂AgInCl₆ powder. For preparing 1 mmol Cs₂Na₁₋ₓAgₓInCl₆, 1 mmol of InCl₃ was first
dissolved in 5 mL 10 M HCl at room temperature, then \( x \) mmol of AgCl and \( 1-x \) mmol of NaCl were added. After several minutes, 2 mmol of CsCl was added and the solution is heated to 115°C. Immediately after the addition of CsCl, a white precipitate forms and the hot solution was held at 115°C for 30 min to ensure a complete reaction. The solid precipitate is then filtered and washed with ethanol before drying it at low pressure.

**Inductively coupled plasma optical emission spectrometry (ICP-OES) measurements:** In this work, ICP-OES measurements were carried out using Agilent 5110. Specifically, for all the materials, weigh 70-100 μg of the sample which is subsequently dissolved in 6.5 mL of hydrochloric acid (HCl, GR, 36-38%, v/v), then transfer the solution to a 25 mL volumetric flask, dilute with ultra-pure water to volume, and mix. Prepare the standard solution (0, 1, 3, 5, 10 mg/L) to measure each elemental’s calibration curve by ICP-OES. Table 3.1 shows an example of the measured Na and Ag concentration in the composition and the computed Na/Ag ratio for our alloyed double perovskite samples \( \text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{InCl}_6 \).

**Table 3.1 ICP-OES results of \( \text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{InCl}_6 \).**

<table>
<thead>
<tr>
<th>Sample Labels</th>
<th>Na (mg/L)</th>
<th>Ag (mg/L)</th>
<th>Na (mmol/L)</th>
<th>Ag (mmol/L)</th>
<th>ICP-OES results</th>
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<td>10</td>
<td>0.44</td>
<td>0.09</td>
<td>/</td>
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<tr>
<td>( \text{Cs}<em>2\text{Na}</em>{0.2}\text{Ag}_{0.8}\text{InCl}_6 )</td>
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<td>46.20</td>
<td>0.12</td>
<td>0.43</td>
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</tr>
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<td>5.55</td>
<td>33.85</td>
<td>0.24</td>
<td>0.31</td>
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<td>0.31</td>
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<td>( \text{Cs}<em>2\text{Na}</em>{0.99}\text{Ag}_{0.01}\text{BiCl}_6 )</td>
</tr>
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</table>

### 3.2 Results and discussion

#### 3.2.1 \( \text{Cs}_2\text{AgInCl}_6 \) and the study on optical properties.

##### 3.2.1.1 Crystal structure of \( \text{Cs}_2\text{AgInCl}_6 \)

To prepare \( \text{Cs}_2\text{AgInCl}_6 \), synthesis method of powders was firstly tried. White powder samples were collected, but a second phase is very easy to form during the synthesis process which should belongs to \( \text{Cs}_2\text{InCl}_5.\text{H}_2\text{O} \) according to PXRD pattern in Figure 3.3a. For this by-product \( \text{Cs}_2\text{InCl}_5.\text{H}_2\text{O} \), it will be further discussed in next chapter since it is also an interesting material.
with broadband yellow emission and the photoluminescence quantum yield could achieve up to 95.5% when Sb is doped.\textsuperscript{25}

After several attempts for synthesizing \( \text{Cs}_2\text{AgInCl}_6 \), the product was improved when the commercial AgCl was replaced by AgCl powder synthesized in lab which made it easily to be dissolved in HCl and totally reacted with other chemicals. From PXRD pattern, the pure phase is shown in Figure 3.3b. The corresponding Rietveld refined results showed a typical double perovskite structure with lattice parameter of \( a = b = c = 10.4805(2) \) Å, consistent with literature report.\textsuperscript{66,174}

\[
\text{Cs}_2\text{AgInCl}_6 \text{ has no solubility in any organic solvent except for DMSO, and the solubility is as low as 0.06 mol/L. So, it is impossible to prepare high quality thin film with the conventional solution process. Luo et al.}^{23} \text{ reported thin film of Bi doped Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6 \text{ fabricated by thermal evaporation and did the electroluminescence measurements. Since thin film preparation is limited in our lab. Small crystal was synthesize for further investigation on excitons and polarons by ultrafast tandem spectroscopy. More details on instrument have been introduced in Chapter 2 for ultrafast tandem spectroscopy.} \]

\( \text{Cs}_2\text{AgInCl}_6 \) experiment
\( \text{Cs}_2\text{AgInCl}_6 \) calculation
\( \text{Cs}_2\text{InCl}_5\times\text{H}_2\text{O} \) calculation

(a)\hspace{3cm} \begin{array}{c}
\text{Normalized intensity (a.u.)} \\
10 15 20 25 30 35 40 45 50 55 60 65 \\
2 \text{Theta (degree)}
\end{array}

Experimental PXRD
Calculated PXRD

(b)\hspace{3cm} \begin{array}{c}
\text{Normalized intensity (a.u.)} \\
10 15 20 25 30 35 40 45 50 55 60 65 \\
2 \text{Theta (degree)}
\end{array}

Experimental PXRD
Calculated PXRD

(c)\hspace{3cm} \begin{array}{c}
\text{Intensity (Counts)} \\
0.0 50.0 100.0 150.0 \\
\text{2-Theta [degrees]}
\end{array}

(d)\hspace{3cm} \begin{array}{c}
\text{Normalized intensity (a.u.)} \\
10 15 20 25 30 35 40 45 50 55 60 65 \\
2 \text{Theta (degree)}
\end{array}

\begin{itemize}
\item \text{Cs}_2\text{AgInCl}_6 \text{ has no solubility in any organic solvent except for DMSO, and the solubility is as low as 0.06 mol/L. So, it is impossible to prepare high quality thin film with the conventional solution process. Luo et al.}^{23} \text{ reported thin film of Bi doped Cs}_2\text{Ag}_{0.60}\text{Na}_{0.40}\text{InCl}_6 \text{ fabricated by thermal evaporation and did the electroluminescence measurements. Since thin film preparation is limited in our lab. Small crystal was synthesize for further investigation on excitons and polarons by ultrafast tandem spectroscopy. More details on instrument have been introduced in Chapter 2 for ultrafast tandem spectroscopy.}
\end{itemize}
3.2.1.2 Optical Properties of Cs$_2$AgInCl$_6$ powder

It is reported that Cs$_2$AgInCl$_6$ has direct band gap but exists parity-forbidden transition due to the same even parity of VBM and CBM at the Γ point$^{118,140,174,180}$. However, the band edge states at the L point have opposite parities, thus, the optical transition is allowed. Furthermore, the band edge optical transitions for the k points between Γ and L are also allowed. So, the fundamental band gap of Cs$_2$AgInCl$_6$ (3.23 eV) could still be defined as the optical gap$^{174}$ but has weak optical absorption coefficients for photons with energies close to the band gap$^{180}$. Nevertheless, Tang’s group$^{118}$ indicated that transitions from a lower level VBM-2 to CBM are also parity-allowed, which is $\sim$1.10 eV larger than the fundamental bandgap between VBM and CBM at the Γ point. According to Filippetti’s calculation, this “absorption gaps” is 3.53 eV$^{140}$.

To determine optical bandgaps for our Cs$_2$AgInCl$_6$ powder, the UV-Vis diffuse reflectance spectra measurements were performed. With Tauc plot the band gaps was extracted for Cs$_2$AgInCl$_6$, a strong absorption edge (3.50ev) and a weak absorption peak(3.21ev) were observed (Figure 3.4a) which is similar to experimental plots in ref. $^{174}$ and ref. $^{182}$. With the femtosecond transient absorption technique, Han$^{182}$ indicated that the weak absorption belongs to parity-forbidden transition.

Figure 3.4 Tauc plots for Cs$_2$AgInCl$_6$ powder (a), PL spectrum of Cs$_2$AgInCl$_6$ powder for three different temperatures (b), Normalized PL decay rates for UV and visible contributions at two different temperatures (c), Normalized PL decay rate of the emission in the visible spectrum (420-670 nm) at different temperatures.
Here, time resolved photoluminescence measurements for Cs$_2$AgInCl$_6$ powder were performed to further understand the electronic transitions. PL spectrum in Figure 3.4b (excited at 330 nm and integrated over the first 5 ns after optical excitation) showed a sharp UV emission (3.21 eV) and a broad emission, centered around 500 nm (2.48 eV). The UV emission roughly corresponds to the onset of significant optical absorption. In addition, as the temperature decreases, the visible emission become more and more intense, at the expenses of the UV emission. Then, the time decay of the two emission ranges is also very different (Figure 3.4c). The UV emission is short-lived, with characteristic picosecond lifetimes at both temperatures. In contrast, the broadband visible emission lives much longer, with an initial decay of nanosecond time scale followed by a long, temperature dependent decay that reach to a fraction of ms at 11 K (Figure 3.4d).

It is well known that photogenerated free carriers normally first form FEs, if the electron–phonon coupling in the perovskite structure is weak, the PL emission originates from the FEs results in a narrow emission spectrum. On the other hand, if the electron–phonon coupling is strong, FEs relax into STEs with an associated surrounding lattice deformation, a broadband emission appears from the recombination through different energy states. The greater lattice distortions in the crystal structure resulted in formation of deeper STE states. These more distorted and deeper trapped states emit lower-energy photons and take longer time to recombine. Excited carriers may shuttle from shallower trapped states to deeper trapped states (Figure 3.5b) which results PL in the red-end emission spectrum turns on more slowly.

Typically, these states are discussed and illustrated by using a configurational coordinate scheme as depicted in Figure 3.5. For an adiabatic excitation from the relaxed ground state (GS), the photogenerated FCs quickly form FEs first (blue arrow) and then relax through FE and STE states. The energy difference between the FE and STE state is the relaxation energy $E_r$, which, together with Huang–Rhys factor “S”, leads to the large Stokes shift between FE emission (blue dotted arrow) and STE emission (gray dotted arrow). In addition, self-trapping generally requires excitons to overcome an energy barrier $E_t$ (trapping energy), simultaneously, the de-trapping of STEs needs to overcome $E_{dt}$. The STEs may decay through radiative or nonradiative recombination processes, resulting in broad emission spectra.
Figure 3.5 Schematic energy diagrams of carrier relaxation processes in the Cs$_2$AgInCl$_6$ structure at room temperature (a) and low temperatures below 200 K (b) (FCs, free carriers; FEs, free excitons; STEs, self-trapped excitons; GS, ground state; $E_t$, trapping energy; $E_{dt}$, detrapping energy of STEs; $E_r$, relaxation energy from FEs to STEs). PL emission is shown with dotted arrow lines.

From experimental observations of Cs$_2$AgInCl$_6$, at room temperature, the PL emission is dominated by a narrow emission which indicates recombination of FEs because the lattice has sufficient thermal energy to de-trapping carriers from STE states back to the FE states. During de-trapping, distorted lattice around STEs can return to its original state through exciton–phonon coupling. Thus, higher temperatures facilitate de-trapping and assist relaxation via a fast non-radiative channel. As the temperature decreases, the de-trapping of STEs back to FE states starts to be difficult since the thermal energy becomes insufficient. So, more carriers stay in STE states resulting in the increase of STE emission intensity. Furthermore, the emission spectra appear red shift at low temperature revealing that more STEs shuttle from shallower trapped states to deeper trapped states. This is also in agreement with the PL lifetime observed in Figure 3.4c, the lifetime doesn’t change with temperature varying for UV emission because of its FEs characteristic, whereas the broadband visible emission lives much longer when the temperature is decreasing since more carriers stay in STE states.

3.2.2 Cs$_2$NaInCl$_6$, Cs$_2$AgBiCl$_6$ and Cs$_2$NaBiCl$_6$

Crystal of Cs$_2$NaInCl$_6$, Cs$_2$AgBiCl$_6$ and Cs$_2$NaBiCl$_6$ were also prepared here with same synthesis method preparing Cs$_2$AgInCl$_6$ crystal, they all have highly symmetric face-centered cubic structures, belong to Fm$3\overline{m}$ space group, consisting of a 3D framework of corner connected octahedra $[\text{B}^{\text{III}}\text{Cl}_6]^{3−}$ or $[\text{B}^{\text{I}}\text{Cl}_6]^{5−}$ (B$^{\text{III}}$=Bi or In; B$^{\text{I}}$=Ag or Na), with Cs$^+$ ions occupying the octahedral external cavities in the framework. The PXRD patterns refinement and Tauc plot of the unalloyed double perovskites are shown in Figure 3.6a-f. The most special one is
Cs$_2$NaBiCl$_6$ whose absorption edge is estimated to be 3.28 eV, followed by a weak absorption band tail extending to 2.93 eV which is more possibly from the defect-related sub-bandgap absorption. The refined lattice parameters and band gaps are summarized in Table 3.2 which are consistent with the previous report. 

Figure 3.6 (a) Rietveld refinement of Cs$_2$NaInCl$_6$, $R_{wp}$ (%) = 11.03, and GOF = 0.16. (b), Rietveld refinement of Cs$_2$AgBiCl$_6$, $R_{wp}$ (%) = 11.71, and GOF = 0.20. (c), Rietveld refinement of Cs$_2$NaBiCl$_6$, $R_{wp}$ (%) = 9.93, and GOF = 0.17. Tauc plot of Cs$_2$NaInCl$_6$ (d), Cs$_2$AgBiCl$_6$ (e) and Cs$_2$NaBiCl$_6$ (f). Photos of synthesized Cs$_2$NaInCl$_6$ crystal (g), Cs$_2$AgBiCl$_6$ crystal (h) and Cs$_2$NaBiCl$_6$ crystal (i).
The crystal size depends on the material, as can be observed from Figure 3.6g-i. Crystal size of Cs$_2$NaInCl$_6$ and Cs$_2$AgBiCl$_6$ is around 50-500 µm while Cs$_2$NaBiCl$_6$ was yellow crystal with the biggest size approaching ~1 cm.

All the four unalloyed double perovskite have limitations in the optoelectronic applications because Cs$_2$AgBiCl$_6$ and Cs$_2$NaBiCl$_6$ possess indirect band gaps while Cs$_2$AgInCl$_6$ and Cs$_2$NaInCl$_6$ have direct band gaps but the dipole transitions between the band edge states are parity-forbidden, which leads to relatively large optical band gaps. However, for alloyed double perovskite compositions, the electronic band structure could be modified which brings very different performances.

### Table 3.2 Crystal information and experimental Band Gap Values for Cs$_2$AgInCl$_6$, Cs$_2$AgBiCl$_6$, Cs$_2$NaInCl$_6$ and Cs$_2$NaBiCl$_6$

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### 3.2.3 Alloyed double perovskite Cs$_2$AgBi$_{1-x}$In$_x$Cl$_6$

Firstly, Bi$^{3+}$/In$^{3+}$ alloyed double perovskites Cs$_2$AgIn$_{1-x}$Bi$_x$Cl$_6$ was synthesized. All the alloyed materials are phase pure and adopt the same Fm$\bar{3}$m space group comparing with parent double perovskites Cs$_2$AgInCl$_6$ and Cs$_2$AgBiCl$_6$. As we can see from X-ray diffraction patterns (Figure 3.7a), Indium and Bismuth was incorporated into the double perovskite, without causing impurities or phase separation, and the compound is completely alloyable by varying
the Bismuth amount from 0 to 100%. Since the ionic radius of In\(^{3+}\) (r(In\(^{3+}\)) = 80 pm) are smaller than those of Bi\(^{3+}\) (r(Bi\(^{3+}\)) = 103 pm), with increasing Bi\(^{3+}\) content the diffraction peak is sequentially shifted to a lower 2θ value as observed in Figure 3.7a for the (400) peak.

The accuracy of In/Bi compositional ratios in the final products were confirmed using the inductively coupled plasma optical emission spectrometry (ICP-OES) technique. And to further analyze the crystal structure of alloyed compositions, the Rietveld analysis of all the samples were conducted using software MAUD\(^{189}\) which extracted the unit cell lattice parameter in Table 3.3. The refinement results of all the samples gave good fit which can be found from appendix. As shown in Figure 3.7b, the refined lattice parameters as a function of Bi content follow Vegard’s Law, linearly increase upon Bi substitution which indicating the uniformly incorporation behavior of In/Bi in crystal.

If we see the photoluminescence quantum yields (PLQYs) of Cs\(_2\)AgIn\(_{1-x}\)Bi\(_x\)Cl\(_6\), Cs\(_2\)AgInCl\(_6\) and Cs\(_2\)AgBiCl\(_6\) both exhibit no luminescence. The direct band gap material Cs\(_2\)AgInCl\(_6\), shows a large optical gap because of the dipole-forbidden while Cs\(_2\)AgBiCl\(_6\) exhibits a parity-allowed transition but possesses indirect band gap, implying unsuitable for efficient PL application.\(^{68}\) As substitution of In\(^{3+}\) with Bi\(^{3+}\) the PLQY starts to increase to 35% when Bi content, \(y = 0.2\) and later sharply reduce to 5% when \(y\) arrives at 0.4 (Figure 3.7c). This could be visually seen in Figure 3.7e when the Cs\(_2\)AgIn\(_{1-x}\)Bi\(_x\)Cl\(_6\) samples was under UV light. Thus, Cs\(_2\)AgIn\(_{1-x}\)Bi\(_x\)Cl\(_6\) shares the merit of direct and parity-allowed transition resulting in high emission efficiency. Meanwhile, as shown in Tauc plot of data (Figure 3.7d), the band gap for Cs\(_2\)AgIn\(_{1-x}\)Bi\(_x\)Cl\(_6\) increases linearly from 2.61 to 2.82 eV as \(y\) decreases from 1 to 0.40 which indicates indirect allowed transition.\(^8\) In contrast, the direct band gap has an exponential decrease from 3.50 to 2.92 for \(y\) values ranging from 0 to 0.25. For Cs\(_2\)AgInCl\(_6\), the valence band maximum (VBM) and conduction band minimum (CBM) originate from Cl-3d/ Ag-4d and In-5s/Ag-5s states, respectively. When Bi starts to be alloyed in Cs\(_2\)AgInCl\(_6\), the interaction of Bi 6s with Cl-3d and Ag-4d states changed the relative contributions from Cl and Ag at the top of the original VBM. The 6s orbital of Bi are higher than the Ag-4d orbital and create a new state above the original VBM.\(^{69}\) On the other hand, as the unoccupied Bi 6p orbitals are higher than the In 5s orbitals, the In 5s-derived CBM is almost not affected by the Bi alloying. Thus, the CBM of the resulting alloyed perovskites are retained, while the VBM are shifted to higher energy levels. And the magnitude of the shift became higher as Bi content increase which explains the exponential decreased band gaps. Therefore, with alloying a moderate amount of Bi (≤25%) into
Cs2AgInCl6, the band gap was reduced, and the parity-forbidden transition is broken while direct band gap structure was retained which cause the PLQY increase. Continue adding Bi, indirect band gap became emerge which leads to the sharp decrease in the PLQY trend line. For the broad white emission of the alloyed Cs2AgIn1-yBiyCl6 materials, it is due to self-trapped excitons originated from the Jahn–Teller distortion which are quite common in metal halide perovskite and allow the emission at lower energy with respect to the absorbed one.23,39,42,54,66,190 Here, as shown from Figure 3.8, the PL spectrum shows red shift when Bi amount is increasing since the bandgap decrease consequently as shown in Figure 3.7d which
results in the formation of deeper STE states that facilitates a larger of Stokes-shift and FWHM.

![Plot](image)

Figure 3.8 PL spectrum of Cs$_2$AgIn$_{1-y}$Bi$_y$Cl$_6$ (nominal compositions)

### 3.2.4 Alloyed double perovskite Cs$_2$Na$_{1-x}$Ag$_x$InCl$_6$

#### 3.2.4.1 Structural properties of Cs$_2$Na$_{1-x}$Ag$_x$Cl$_6$ and Cs$_2$Na$_{1-x}$Ag$_x$In$_{0.99}$Bi$_{0.01}$Cl$_6$

Now, let us see another two series of alloyed double perovskite compositions, Cs$_2$Na$_{1-x}$Ag$_x$Cl$_6$ and Cs$_2$Na$_{1-x}$Ag$_x$In$_{0.99}$Bi$_{0.01}$Cl$_6$. As shown in Figure 3.9a and b, XRD patterns of the as-synthesized products contained no additional impurity phase, and with respect to Cs$_2$Na$_{1-x}$Ag$_x$In$_{0.99}$Bi$_{0.01}$Cl$_6$, additional 1% alloyed Bi doesn’t affect the crystal structure. By increasing the sodium content, we could observe the (422) peaks shift to lower 2θ values because of the larger Na$^+$ radius than that of Ag$^+$ (Na$^+$ 166 pm, Ag$^+$ 145 pm). Another obvious evidence for verifying the alloying was the enhanced intensity of (111) diffraction peaks around 14.6° upon increasing Na content. It was observed that Cs$_2$NaInCl$_6$ exhibited a strong (111) peak and Cs$_2$AgInCl$_6$ contained almost negligible (111) peak. As the introduction of Na$^+$ in the lattice, the gradual increase of (111) diffraction peak strongly verified the alloying both in the two system materials.[23] The accurate compositional ratios in the final products were measured by ICP-OES technique and listed in Table 3.3 where the lattice parameters can also be found for all these samples. And the lattice parameter of both Cs$_2$Na$_{1-x}$Ag$_x$Cl$_6$ and Cs$_2$Na$_{1-x}$Ag$_x$In$_{0.99}$Bi$_{0.01}$Cl$_6$ follows Vegard’s Law, linearly decrease upon Ag substitution which denotes Na/Ag was incorporated uniformly in crystal (Figure 3.9c). These are evidence that the actual element contents in the corresponding alloyed compounds fit well with the nominal contents.
Interestingly, the PLQY of the alloyed Cs$_2$Na$_{1-x}$Ag$_x$Cl$_6$ materials is quite low with the highest at 12% when Ag content $x=0.78$. However, the addition of a small fraction of bismuth, namely 1%, changes completely the perovkite’s behaviour and tremendously improve the emission properties. The PLQY of Cs$_2$Na$_{1-x}$Ag$_x$In$_{0.99}$Bi$_{0.01}$Cl$_6$ is much higher and it reaches 97% for the composition with 61% of sodium and 39% of silver (Figure 3.9d).
3.2.4.2 Optical properties of Cs$_2$Na$_{1-x}$Ag$_x$Cl$_6$ and Cs$_2$Na$_{1-x}$Ag$_x$In$_{0.99}$Bi$_{0.01}$Cl$_6$

Figure 3.10 PL spectrum of Cs$_2$Na$_{1-x}$Ag$_x$InCl$_6$ (a) and Cs$_2$Na$_{1-x}$Ag$_x$In$_{0.99}$Bi$_{0.01}$Cl$_6$ (b). The absorption spectra of the 1% Bi-alloyed and no Bi alloyed Cs$_2$Na$_{0.6}$Ag$_{0.4}$InCl$_6$ samples (c). Optical transitions of a Bi$^{3+}$ ion (d).

As can be observed in Figure 3.10a and b, the emission spectrum of all these materials actually almost didn’t change, no matter the Na/Ag ratios changes or the Bismuth was added although the PLQY varies a lot, which indicated that this broad warm-white emission originated from STEs. And the addition of Bi$^{3+}$ can significantly enhance the PL intensity from “dark” STEs by forming a sub-band and increasing the lattice distortion as illustrated above.

The absorption spectra of the composition Cs$_2$Na$_{0.6}$Ag$_{0.4}$InCl$_6$ with no Bi and with 1% Bi alloyed show an additional peak at ∼375nm while the absorption is not significant in the visible range as we can see in the plot of Figure 3.10c. Herein, as a $ns^2$ ion, it features a characteristic of $6s^2 \rightarrow 6s^1p^1$ absorption transitions of the [BiCl$_6$]$^{3-}$ octahedra$^{41,68,192}$. Thus, the new optical absorption with a peak range from 360 to 400 nm is attributed to $^1S_0 \rightarrow ^3P_1$ transition of the Bi$^{3+}$ ion while the emission obtained is assigned to the $^3P_1 \rightarrow ^1S_0$ transition.
3.2.4.3 Tandem spectroscopy of $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{Cl}_6$ and $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{In}_{0.99}\text{Bi}_{0.01}\text{Cl}_6$

The role of Bismuth was studied by tandem spectroscopy, in this method, time-resolved photoluminescence (TRPL) and transient absorption (TA) could be measured at the same spot of sample as introduced in chapter 2.

Figure 3.11 (a) Streak camera image of $\text{Cs}_2\text{Na}_{0.6}\text{Ag}_{0.4}\text{InCl}_6$ samples (up), $\text{Cs}_2\text{Na}_{0.6}\text{Ag}_{0.4}\text{In}_{0.99}\text{Bi}_{0.01}\text{Cl}_6$ (bottom) and their PL spectrum (middle). (b) Photoinduced absorption of $\text{Cs}_2\text{Na}_{0.6}\text{Ag}_{0.4}\text{InCl}_6$ samples (blue) and $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{In}_{0.99}\text{Bi}_{0.01}\text{Cl}_6$ (red). (c) Comparison of TRPL time decay between $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{InCl}_6$ (black line) and $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{In}_{0.99}\text{Bi}_{0.01}\text{Cl}_6$ (red line). (d) Comparison of TA time decay between $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{InCl}_6$ (black line) and $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{In}_{0.99}\text{Bi}_{0.01}\text{Cl}_6$ (blue line). (e) Comparison of TRPL time decay (red line) and TA time decay (blue line) for $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{InCl}_6$. (f) Comparison of TRPL time decay (red line) and TA time decay (blue line) for $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{In}_{0.99}\text{Bi}_{0.01}\text{Cl}_6$. Noted that here all the element ratio in compositions round one decimal place.
Here firstly, the measurements for the highest quantum yield composition $\text{Cs}_2\text{Na}_{0.6}\text{Ag}_{0.4}\text{In}_{0.99}\text{Bi}_{0.01}\text{Cl}_6$ and its host material $\text{Cs}_2\text{Na}_{0.6}\text{Ag}_{0.4}\text{InCl}_6$ are shown in Figure 3.11a and b. The emission spectrum from TRPL doesn’t change with the addition of Bismuth. And a photoinduced absorption could be observed in the pump-probe measurement.

Then, the PL lifetime and TA decay time between $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{Cl}_6$ and $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{In}_{0.99}\text{Bi}_{0.01}\text{Cl}_6$ were compared which can be found in Figure 3.11c and d. The PL lifetime is long and basically the same for all the Na/Ag alloyed samples both without Bi and with 1% Bi while the TA decay time is quite different since it is longer for the compositions without bismuth which can be explained by the presence of defects like traps that make the emission not efficient.

Furthermore, comparison of PL lifetime and TA decay time for $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{Cl}_6$ and $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{In}_0.99\text{Bi}_{0.01}\text{Cl}_6$ was shown in Figure 3.11e and f separately. Remarkably, for the Bi doped sample with high PLQY, the TA decay time is comparable to the PL lifetime which is compatible with the fact that optical excitations are captured by the presence of new states above the VBM instead of being trapped by defects, so the recombination is totally radiative.

3.2.4.4 Varying Bi content in $\text{Cs}_2\text{Na}_{0.6}\text{Ag}_{0.4}\text{In}_{1-y}\text{Bi}_y\text{Cl}_6$

Then, the host material $\text{Cs}_2\text{Na}_{0.6}\text{Ag}_{0.4}\text{InCl}_6$ was focused on to perform a systematic analysis on the Bi fraction ranging from 10% to $10^{-6}$ % to understand the effect of Bi. We can see that a minimum amount of bismuth is needed to create new states that funnel the excitations and it appears to be 0.1 % (Figure 3.12a). Such small amount of Bi is clearly not enough to alter the oscillator strength of the optical transitions in the crystals. Moreover, 1% Bi alloying could bring the highest PLQY whereas continue adding more Bi will start to reduce the quantum yield because of the self-quenching effect, which is a typical character of ionoluminescence.$^{192}$

In general, in order to obtain the best luminescence efficiency for a phosphor, the concentration of the activator in the host material must be as high as possible. If the concentration of the dopant is low enough to obtain good luminescence (critical concentration), the dopant ion can be considered as an isolated center in the host system. However, with the increase of the dopant concentration, the ion centers become close to each other, and strong interaction between two activators is capable of transferring excitation energy from one to the other resulting in energy lost to the surface, disturbances, or impurities, i.e. self-quenching. Therefore, under high activator concentration, the
probability for energy transfer between activators is greater than that of emission and does not contribute to the luminescence. So, the emission efficiency exhibits decreasing when the amount of activator is higher than critical concentration.\textsuperscript{193}

![Graph showing emission efficiency vs Bi content](image)

Figure 3.12 (a) PLQY, (b) PL spectrum and (c) Comparison of TRPL time decay (red line) and TA time decay (blue line) for Cs\textsubscript{2}Na\textsubscript{0.6}Ag\textsubscript{0.4}InCl\textsubscript{6} alloyed with variant amount of Bi. Noted that the addition of Bi here are all nominal amounts.

There is no difference in the emission spectra except in the presence of the high percentage of Bismuth (>2%) which red-shifts the emission (Figure 3.12b). However, the comparison of PL lifetime and TA decay time in Figure 3.12c shows that, the Bi alloyed sample possesses higher emission efficiency if the TA decay time is more comparable to the PL lifetime, and the Bismuth states above the VBM are directly responsible for this since it brightens the dark
excitons that are already present in the Bismuth free compounds. This is totally consistent with the illustration above, this broad band white emission originate from STEs caused by Jahn–Teller distortion while Bi can facilitate this distortion to form deeper states and create red shift of the emission.

3.2.4.5 Stability of Cs$_2$Na$_{1-x}$Ag$_x$In$_{0.99}$Bi$_{0.01}$Cl$_6$

It is worth noting that all the double perovskite compounds here show impressive thermal and water stability due to its inorganic nature and can even resist to water immersion. As shown in Figure 3.13a, Cs$_2$Na$_{0.83}$Ag$_{0.17}$In$_{0.99}$Bi$_{0.01}$Cl$_6$ retained strong warm white emission under 365 nm UV light even after 3h immersed in deionized water. Figure 3.13b shows the photo of Cs$_2$Na$_{0.83}$Ag$_{0.17}$In$_{0.99}$Bi$_{0.01}$Cl$_6$ which was dried after immersed in deionized water, preserving 85% of the original PLQY after 3h soaking and half an hour UV irradiation and XRD characterization revealed the presence of a small amount of second phase appeared.

![Figure 3.13](image)

Figure 3.13 (a) Photos of the Cs$_2$Na$_{0.83}$Ag$_{0.17}$In$_{0.99}$Bi$_{0.01}$Cl$_6$ sample immersed in deionized water and (b) its evaporated sample. (c) Comparison of PXRD patterns for them.

3.2.5 Alloyed double perovskite Cs$_2$NaIn$_{1-y}$Bi$_y$Cl$_6$

3.2.5.1 Properties of Cs$_2$NaIn$_{1-y}$Bi$_y$Cl$_6$ and Cs$_2$Na$_{0.99}$Ag$_{0.01}$In$_{1-y}$Bi$_y$Cl$_6$

Strikingly, the behavior is quite different for compound that use alloyed In/Bi as trivalent cations with only Na as monovalent cation. As we can see from Figure 3.14, in the case of
materials with no Ag but trivalent cation is a mixture of In and Bi, there is no emission or very low emission under UV light. However, the addition of 1% of Ag to these compounds increases dramatically the emission in the visible range and the color changes from warm white to orange with raising the amount of Bi.

Figure 3.14 Nominal compositions of Cs2NaIn1-yBiyCl6 (top) and Cs2Na0.99Ag0.01In1-yBiyCl6 (bottom) under UV light. PXRD patterns and lattice parameter of Cs2NaIn1-yBiyCl6 and Cs2Na0.99Ag0.01In1-yBiyCl6 in Figure 3.15a-d confirmed the pure phase and uniform alloyed structure. The ICP-OES results (Table 3.3) show that although the feeding amount of all ingredients is strictly carried out in accordance with the nominal compositions, obviously, the ratio of Indium and Bismuth in final alloyed products is always higher than in the nominal compositions.
The PLQY results in Figure 3.15(e) corroborated the emission efficiency of compounds under UV light. The highest quantum yield reaches 84% for the composition with 31% of Bi and 69% In, while it is basically zero for all the samples without silver except the one with 100% of bismuth. In this case the increasing amount of bismuth makes the emission red-shift as we can see in the plot of Figure 3.15(f).

Now, let us focus on the comparison of compound with highest quantum yield and its host material which are Cs$_2$Na$_{0.99}$Ag$_{0.01}$In$_{0.7}$Bi$_{0.3}$Cl$_6$ and Cs$_2$NaIn$_{0.3}$Bi$_{0.7}$Cl$_6$ respectively. The dynamics of optical gain in these two samples were studied through a streak camera in Figure 3.16a.

The emission spectrum in the sample without silver shows an additional emission in the blue range which disappears after the addition of silver. PL lifetime was measured both at blue range and visible range in Figure 3.16b. For Cs$_2$NaIn$_{0.7}$Bi$_{0.3}$Cl$_6$, the shorter wavelength components rapidly decay in nanosecond timescale, whereas longer wavelength components decay much more slowly. This could be explained as a rapidly relaxation from higher vibrational energy states to lower energy states after the compound are excited, which have
lifetimes of a few nanoseconds. However, the behavior is quite different when 1% Ag was added into Cs$_2$NaIn$_{0.7}$Bi$_{0.3}$Cl$_6$, the decay time in both blue range and visible range are much long which is consistent with the results in TA decay time plot. There is a very fast decay in the short initial time for Cs$_2$NaIn$_{0.7}$Bi$_{0.3}$Cl$_6$ while no initial fast decay for Cs$_2$Na$_{0.99}$Ag$_{0.01}$In$_{0.7}$Bi$_{0.3}$Cl$_6$ (Figure 3.16c). This can be explained that, as the Ag is added, after excitation, holes are quickly trapped at [AgCl$_6$] octahedra and the electronic configuration of Ag was changed consequently, causing a strong Jahn–Teller distortion and create self trapped excitons emission which has longer lifetime.

![Streak camera image of compositions Cs$_2$NaIn$_{0.7}$Bi$_{0.3}$Cl$_6$ (up), Cs$_2$Na$_{0.99}$Ag$_{0.01}$In$_{0.7}$Bi$_{0.3}$Cl$_6$ (bottom) and their PL spectrum (middle). (b) TRPL time decay: Cs$_2$NaIn$_{0.7}$Bi$_{0.3}$Cl$_6$ (dark blue line) and Cs$_2$Na$_{0.99}$Ag$_{0.01}$In$_{0.7}$Bi$_{0.3}$Cl$_6$ (light blue line) in blue range; Cs$_2$NaIn$_{0.7}$Bi$_{0.3}$Cl$_6$ (dark red line) and Cs$_2$Na$_{0.99}$Ag$_{0.01}$In$_{0.7}$Bi$_{0.3}$Cl$_6$ (light red line) in visible range. (c) TA time decay of Cs$_2$NaIn$_{0.7}$Bi$_{0.3}$Cl$_6$ (black line) and Cs$_2$Na$_{0.99}$Ag$_{0.01}$In$_{0.7}$Bi$_{0.3}$Cl$_6$ (purple line).](image)

It exhibits similar behavior for Cs$_2$NaBiCl$_6$ as it has emission in blue range which is negligible after the addition of 1% Ag (Figure 3.17a). Then, a systematic analysis on the Ag fraction ranging from $10^{-3}$ % to 10% was further performed. The emission range doesn’t change with variable addition of Ag (Figure 3.17d) and again we can see a limit in the minimum amount of
silver needed to activate the efficient emission which is about 0.1% (Figure 3.17c) at which the TA initial fast decay started to disappear and the TA decay time becomes much comparable to the PL lifetime which indicates more bright excitons and higher emission efficiency (Figure 3.17b). At high Ag concentration, because of self-quenching, both TA and PL decay faster while the emission efficiency exhibits decreasing.

![Figure 3.17](image)

Figure 3.17 (a) Streak camera image of compositions Cs$_2$NaBiCl$_6$ (up), Cs$_2$Na$_{0.99}$Ag$_{0.01}$BiCl$_6$ (bottom) and their PL spectrum (middle). (b) Comparison of TRPL time decay (red line) and TA time decay (blue line), (c) PLQY and (d) PL spectrum for Cs$_2$NaBiCl$_6$ alloyed with variant amount of Bi. Noted that the addition of Ag here are all nominal amounts.

Continue adding Ag content, Figure 3.18 shows photo of the nominal alloyed materials Cs$_2$Na$_1-x$Ag$_x$BiCl$_6$ under UV light. According to the reports both Cs$_2$NaBiCl$_6$ and Cs$_2$AgBiCl$_6$ possess indirect bandgap$^{8,84,124,186}$, the mechanism for this orange emission is deserved to be further studied in the future work.
Figure 3.18 (a), Photo of nominal alloyed Cs$_2$Na$_{1-x}$Ag$_x$BiCl$_6$ samples under UV light. (b), PXRD pattern of alloyed Cs$_2$Na$_{1-x}$Ag$_x$BiCl$_6$ samples.

Table 3.3 Inductively coupled plasma optical emission spectrometer (ICP-OES) results and lattice parameter (extracted from MAUD) of crystal sample Cs$_2$Na$_{1-x}$Ag$_x$In$_{1-y}$Bi$_y$Cl$_6$.

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>ICP-OES results</th>
<th>Refined lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
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<td>Cs$<em>2$AgIn$</em>{0.2}$Bi$_{0.8}$Cl$_6$</td>
<td>10.7121</td>
</tr>
<tr>
<td>Cs$_2$AgBiCl$_6$</td>
<td>Cs$_2$AgBiCl$_6$</td>
<td>10.7754</td>
</tr>
</tbody>
</table>

| Cs$_2$Na$_{1-x}$Ag$_x$In$_{1-y}$Bi$_y$Cl$_6$ & Cs$_2$Na$_{1-x}$Ag$_x$In$_{0.99}$Bi$_{0.01}$Cl$_6$ |
|-----------------------------------------------|-----------------------------------------------|
| Cs$_2$Na$_{0.2}$Ag$_{0.8}$In$_{0.0}$Cl$_6$    | Cs$_2$Na$_{0.2}$Ag$_{0.8}$In$_{0.0}$Cl$_6$    | 10.4898 |
| Cs$_2$Na$_{0.4}$Ag$_{0.6}$In$_{0.0}$Cl$_6$    | Cs$_2$Na$_{0.4}$Ag$_{0.6}$In$_{0.0}$Cl$_6$    | 10.5019 |
| Cs$_2$Na$_{0.6}$Ag$_{0.4}$In$_{0.0}$Cl$_6$    | Cs$_2$Na$_{0.6}$Ag$_{0.4}$In$_{0.0}$Cl$_6$    | 10.5073 |
| Cs$_2$Na$_{0.8}$Ag$_{0.2}$In$_{0.0}$Cl$_6$    | Cs$_2$Na$_{0.8}$Ag$_{0.2}$In$_{0.0}$Cl$_6$    | 10.5096 |
| Cs$_2$Na$_{1.0}$Ag$_{0.0}$In$_{0.0}$Cl$_6$    | Cs$_2$Na$_{1.0}$Ag$_{0.0}$In$_{0.0}$Cl$_6$    | 10.5236 |
| Cs$_2$NaInCl$_6$ | Cs$_2$NaInCl$_6$ | 10.5325 |
| Cs$_2$AgIn$_{0.99}$Bi$_{0.01}$Cl$_6$ | Cs$_2$AgIn$_{0.99}$Bi$_{0.01}$Cl$_6$ | 10.4830 |
| Cs$_2$Na$_{0.2}$Ag$_{0.8}$In$_{0.99}$Bi$_{0.01}$Cl$_6$ | Cs$_2$Na$_{0.2}$Ag$_{0.8}$In$_{0.99}$Bi$_{0.01}$Cl$_6$ | 10.4939 |
| Cs$_2$Na$_{0.4}$Ag$_{0.6}$In$_{0.99}$Bi$_{0.01}$Cl$_6$ | Cs$_2$Na$_{0.4}$Ag$_{0.6}$In$_{0.99}$Bi$_{0.01}$Cl$_6$ | 10.5059 |
| Cs$_2$Na$_{0.6}$Ag$_{0.4}$In$_{0.99}$Bi$_{0.01}$Cl$_6$ | Cs$_2$Na$_{0.6}$Ag$_{0.4}$In$_{0.99}$Bi$_{0.01}$Cl$_6$ | 10.5068 |
| Cs$_2$Na$_{0.8}$Ag$_{0.2}$In$_{0.99}$Bi$_{0.01}$Cl$_6$ | Cs$_2$Na$_{0.8}$Ag$_{0.2}$In$_{0.99}$Bi$_{0.01}$Cl$_6$ | 10.5157 |
| Cs$_2$Na$_{1.0}$Ag$_{0.0}$In$_{0.99}$Bi$_{0.01}$Cl$_6$ | Cs$_2$Na$_{1.0}$Ag$_{0.0}$In$_{0.99}$Bi$_{0.01}$Cl$_6$ | 10.5256 |
| Cs$_2$Na$_{0.99}$Ag$_{0.01}$In$_{0.99}$Bi$_{0.01}$Cl$_6$ | Cs$_2$Na$_{0.99}$Ag$_{0.01}$In$_{0.99}$Bi$_{0.01}$Cl$_6$ | 10.5346 |
| Cs$_2$NaIn$_{0.99}$Bi$_{0.01}$Cl$_6$ | Cs$_2$NaIn$_{0.99}$Bi$_{0.01}$Cl$_6$ | 10.5347 |
3.3 Powder of alloyed double perovskite Cs$_2$Na$_{1-x}$Ag$_x$InCl$_6$

As mentioned above, crystals of 1% Bi doped Cs$_2$Na$_{1-x}$Ag$_x$InCl$_6$ exhibit highly efficient warm white emission. Here, powders for these compositions were also prepared, and it is found that the optical properties of powders are quite different from that of crystal samples. Figure 3.19a-c shows the PXRD patterns and cubic crystal lattice parameter as a function of Ag content for powder samples Cs$_2$Na$_{1-x}$Ag$_x$InCl$_6$ and Cs$_2$Na$_{1-x}$Ag$_x$In$_{0.99}$Bi$_{0.01}$Cl$_6$ which indicated the compounds are completely alloyable by varying the Ag amount from 0 to 100%. All the samples are white powder as shown in Figure 3.19d. This is different from crystal samples which show different color when the composition varies (Figure 3.20a). The color of these crystal samples was assumed to be color centers caused by lattice disorder.\(^{194,195}\)
Figure 3.19 PXRD patterns of powders samples Cs\textsubscript{2}Na\textsubscript{1-x}Ag\textsubscript{x}InCl\textsubscript{6} (a) and Cs\textsubscript{2}Na\textsubscript{1-x}Ag\textsubscript{x}In\textsubscript{0.99}Bi\textsubscript{0.01}Cl\textsubscript{6} (b) with different Na/Ag ratio, the asterisk marks the (111) diffraction peak. (c) The cubic crystal lattice parameter as a function of Ag content. The black dash line shows a Vegard’s Law fit. (d) White powder of alloyed double perovskite samples.

From Figure 3.20b, we can observe that the PXRD patterns of powder samples and crystal samples are nearly identical, except that the powder show smaller FWHM, suggesting a better crystallinity. An increase in stacking faults and structural disorder could widen the XRD peaks\textsuperscript{196}. And the increasing in hardness and density of point defects may affect the crystallinity and grain boundary mobility, which causes a linear increase in the FWHM of XRD peak\textsuperscript{197}.
The PLQY of powders and crystals are quite different, especially for Cs$_2$Na$_{1-x}$Ag$_x$InCl$_6$ compositions as there is no logical trend for its value of PLQY. In addition, for the 1% Bi alloyed materials, powders also show a more excellent performance than crystals in PLQY. For this part, I am interested in discovering the relation between the lattice environment (e.g. defects or disorder) and the optical property, and more works need to be done in the future.

Table 3.4 Inductively coupled plasma optical emission spectrometer (ICP-OES) results and lattice parameter (extracted from MAUD) of powder sample Cs$_2$Na$_{1-x}$Ag$_x$In$_{0.99}$Bi$_{0.01}$Cl$_6$

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>ICP-OES results</th>
<th>Refined lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$_2$AgInCl$_6$</td>
<td>Cs$_2$AgInCl$_6$</td>
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<td>10.5366</td>
</tr>
</tbody>
</table>
3.4 Conclusions

In this chapter, firstly, four double perovskite materials $\text{Cs}_2\text{AgInCl}_6$, $\text{Cs}_2\text{NaInCl}_6$, $\text{Cs}_2\text{AgBiCl}_6$ and $\text{Cs}_2\text{NaBiCl}_6$ were synthesized. Wherein, optical property of $\text{Cs}_2\text{AgInCl}_6$ was deeply investigated when the PL spectrum showed both a sharp UV emission and a broad emission with a trade-off relation as the temperature is changing which is originated from de-trapping. The broad emission is attributed to self-trapped excitons, but the PLQY is extremely low. Then the alloyed $\text{Cs}_2\text{Ag}_{1-x}\text{Na}_x\text{Bi}_{1-y}\text{In}_y\text{Cl}_6$ double perovskite materials were systematically studied which exhibit extremely highly efficient warm white light emission and moisture resistant. It is demonstrated that the the white emission is clearly produced by self-trapped excitons which are characteristic of these compounds, but such outstanding emission properties are due to the simultaneous presence of Bi and Ag.

The addition of a small amount of Bi and Ag in the sodium indium-based material seems to be fundamental on the production of bright excitons which are already present in the undoped compound, but with a lower density so the total PLQY is low.

The quantum yield of compositions without Bi or Ag is low, and it starts to become high with the presence of less than 1% of these dopants. According to the time-resolved measurements, it is reasonable to state that it is related to the addition of proper sites that funnel the excited states which radiatively recombine with an efficiency close to 100%. And it seems that the crystal lattice environment (e.g. defects and disorder) also affects the PLQY which need to be further studied.
CHAPTER 4 Exploratory synthesis of double perovskites

In last chapter, I focused on the warm white emission with alloyed double perovskites $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{In}_y\text{Bi}_{1-y}\text{Cl}_6$. In this chapter, I further explore more different kinds of double perovskite materials which are synthesized with several varied synthesis methods. Except for solution synthesis for preparing both powder samples and crystal samples (with size of 200μm-1cm), mechanochemical approach and solid-state synthesis were also attempted here. In addition, the optical property of them were also studied for evaluating its potential and, hopefully the feasibility in optoelectronic applications.

We know that, because of parity forbidden, $\text{Cs}_2\text{AgInCl}_6$ possesses a wide direct band gap. Thus, $\text{Cs}_2\text{AgInBr}_6$ is expected to have a smaller bandgap ($2.36 \text{ eV}$), however, it is very hard to be synthesized as the phase $\text{Cs}_2\text{InBr}_5\cdot\text{H}_2\text{O}$ is favourable instead of phase $\text{Cs}_2\text{AgInBr}_6$. So, I tried to synthesize $\text{MA}_2\text{AgInBr}_6$, but the material actually belongs to the trigonal system and has a space group $P\text{3}m\text{1}$. $\text{Cs}_2\text{CuInCl}_6$ was suggested with calculated bandgap as low as $\sim1\text{eV}$ whereas it is reported not stable since $[\text{CuCl}_6]$ octahedra with sixfold coordination is not energetically favourable comparing to $[\text{CuCl}_4]$ tetrahedra. In fact, according to our synthesis, it is believed that $\text{Cs}_2\text{CuInCl}_6$ can also be stable in several strict conditions.

$\text{Cs}_2\text{AgBiBr}_6$ has indirect band gaps of $2.07 \text{ eV}$. In/Bi alloyed compounds $\text{Cs}_2\text{AgIn}_{1-x}\text{Bi}_x\text{Br}_6$ were tried to tune the convergence of direct and indirect bandgaps. However, the product is demonstrated to be $\text{Cs}_2\text{InBr}_5\cdot\text{H}_2\text{O}$ when Indium content is $\geq0.5$ with the synthesis method for preparing crystal.

Considering the negative decomposition energy of $\text{Cs}_2\text{AgBiI}_6$ ($\text{Cs}_2\text{AgBiI}_6 \rightarrow 1/2 \text{CsAgI}_3 + 1/2 \text{Cs}_3\text{Bi}_2\text{I}_6$), I attempted to prepare $\text{MA}_2\text{AgBiI}_6$ to gain a smaller band gap iodide double perovskite material. Whereas the final product was recognized as $\text{MA}_3\text{Bi}_2\text{I}_6$.

Meanwhile, Sb alloyed $\text{Cs}_2\text{NaInCl}_6$ was studied which exhibits blue emission under UV excitation. And the blue emission can be ascribed to localized Sb$^{3+}$ excited state relaxation via a $^3\text{P}_1 \rightarrow ^1\text{S}_0$ pathway. Sb alloyed $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ shows yellow emission under UV light whereas it becomes blue-green emission when the host material experienced conversion of $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ to $\text{Cs}_3\text{InCl}_6$. Furthermore, Sb alloying in $\text{Cs}_2\text{NaInCl}_6$, $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ and $\text{Cs}_3\text{InCl}_6$ were compared, and it comes to the conclusion that, the greater degree of Jahn–Teller distortion, the more red-shifted of the STEs emission and the longer the STEs lifetime.
4.1 Experiments

Chemicals. Caesium chloride (CsCl, 99.999%), silver nitrate (AgNO₃, 99.9%), indium chloride (InCl₃, 99.999%), indium oxide (In₂O₃, 99.95%), antimony oxide (Sb₂O₃, 99.9%), acetonitrile (CH₃CN, 99.8%), hydrochloric acid (HCl, 37%) were purchased from Alfa Aesar. Sodium chloride (NaCl, >99%), bismuth chloride (BiCl₃, 99.9%), bismuth oxide (Bi₂O₃, 99.9%), potassium bromide (KBr, >99%), hydrobromic acid (HBr, 48%), antimony chloride (SbCl₃, >99.95%) were purchased from Sigma Aldrich. Potassium chloride (KCl, >99.5%) were purchased from Merck & Co. Methylammonium bromide (MABr, >99.99%) and Methylammonium iodide (MAI, >99.99%) were purchased from Greatcell Solar Materials Pty Ltd. AgCl and AgBr were precipitated from as prepared aqueous solutions of AgNO₃ and KCl or KBr.

Synthesis method 1: The synthesis of Cs₂AgBiBr₆ crystal was achieved following the solution precipitation strategy as reported previously while the hygroscopic metal bromides were replaced by stable metal oxides. Briefly, 0.5 mmol Bi₂O₃ was added in 10 mL of HBr (48% w/w) and stirred under 110°C to fully dissolve the solids. 2.00 mmol CsBr and 1.00 mmol AgBr were then successively added to the solution and heated to 130 °C. The solution was held at 130 °C for 2 h and then cooled to room temperature. Small crystals of duller red came out from solution upon sitting at room temperature overnight. These crystals were filtered, washed with ethanol, and dried under reduced pressure.

Synthesis method 2: This synthesis method is the same for preparing Cs₂AgInCl₆ crystal which has already been introduced in last chapter. Here, Cs₂AgInBr₆, Cs₂InCl₅·H₂O, Cs₃InCl₆, Sb alloyed Cs₂NaInCl₆ and alloyed materials Cs₂Na₁₋ₓAgₓBiCl₆ etc. are all used by this method while the starting chemicals varies according to the final products.

Synthesis method 3: The Cs₂AgInBr₆ compounds were successfully obtained through a process introduced by Cheng et al. Weighed 1mmol CsBr, 0.5mmol InBr₃ and 0.5mmol AgBr in the mortar and fully ground and mixed them in a nitrogen glove box. The solid powders were sealed in quartz tube under vacuum and heated to 200 °C for 2 hours. For MA₂AgInBr₆, it is prepared by the same synthesis method except that CsBr was substituted by MABr. For MA₂AgBiI₆, the starting chemicals were 2mmol MAI, 1mmol BiI₃ and 1mmol AgI.
**Synthesis method 4**: The Cs$_2$CuInCl$_6$ was prepared according to reported method from Kanatzidis et al$^{200}$. An amount of 0.5mmol of CuCl and 0.5mmol InCl$_3$ were dissolved in 3.4 mL HCl (37%) and 0.85 mL H$_3$PO$_2$ (50%) at room temperature. Then 1mmol CsCl was added, and the solution was heated to 105 °C. The solution was held at 105 °C for 20 min and then the solid precipitate is filtered and washed with ethanol before drying it at low pressure.

### 4.2 Results and discussion

#### 4.2.1 Cs$_2$AgInBr$_6$ and MA$_2$AgInBr$_6$

Band gaps can be tuned through replacement with halogen atoms (iodine, I; bromine, Br and chloride, Cl)$^{201}$. With given cations, the bandgap decreases with the increasing of X anion radii, that is $E_g$(Cl) > $E_g$(Br) > $E_g$(I). Since Cs$_2$AgInCl$_6$ exhibits a large band gap (3.5 eV), Cs$_2$AgInBr$_6$ was expected to be synthesized which may have band gap of 2.1 eV according to the calculations$^{140}$. Firstly, synthesis method 2 and synthesis method 4 were both tried to obtain Cs$_2$AgInBr$_6$, however, PXRD patterns showed that we failed on both the products (Figure 4.2a, b). Notably, PXRD patterns of these two products are very similar and both fit well with that of Cs$_2$InBr$_5$·H$_2$O (Figure 4.2c, d).$^{202}$

![Figure 4.2 Synthesis process of method 3](image)
Breternitz et al. reported the successful synthesis of Cs$_2$AgInBr$_6$ as bulk powder using a mechanochemical approach$^{137}$. It has a cubic elpasolite-type structure and crystallize in the space group Fm$\overline{3}$m with cell parameter of $a = 11.00$ Å. The compound has direct optical bandgap of 2.36 eV. Then Cs$_2$AgInBr$_6$ was tried to prepare using the planetary ball mill. However, since CsBr and InBr$_3$ is highly hygroscopic, the sample mixture took on moisture from the air while being ground, causing the sample to clump together in a gray mass that had the appearance of wet clay. In addition, according to Breternitz’s work, Cs$_2$AgInBr$_6$ degrades very quickly under light illumination which is a significant challenge for application in photovoltaics.

Then it is wondered whether the compound could be more stable if cation Cs$^+$ of compound is substituted by organic cation CH$_3$NH$_3^+$ (methylammonium or MA). And thus, MA$_2$AgInBr$_6$ was synthesized by solid state synthesis with method 4. However, the PXRD pattern is comparable to the calculation of reference$^{203}$ which shows this product belongs to the trigonal system and has a space group $P\overline{3}m1$ (Figure 4.4a). It exhibits a 1-dimensional chain.

Figure 4.2 PXRD pattern of Cs$_2$AgInBr$_6$ prepared by synthesis method 1 (a) and synthesis method 4 (b), PXRD pattern comparison of Cs$_2$AgInBr$_6$ prepared by synthesis method 1 and synthesis method 4 (c), PXRD pattern of Cs$_2$InBr$_5$.H$_2$O

Figure 4.3 Mechanoynthesis process of Cs$_2$AgInBr$_6$
of face-sharing alternating octahedra of [AgBr$_6$]$^{5-}$ and [InBr$_6$]$^{3-}$ and the MA cations are located in the empty space formed between the chains. And the absorption onset in Figure 4.4b exhibits a wide band gap in the UV range for (MA)$_2$AgInBr$_6$ which is consistent with the report value 3.89 eV$^{203}$.

Figure 4.4 PXRD pattern of MA$_2$AgInBr$_6$ (a) (insert photo is the synthesized MA$_2$AgInBr$_6$ and the 1-D chains of face-sharing AgBr$_6$ and InBr$_6$ octahedra and MA units) and UV-Vis absorption spectra (b)

### 4.2.2 Cs$_2$CuInCl$_6$

Theoretical studies have shown that the proposed Cu(I)-based halide double perovskites exhibit bandgaps that are almost 1 eV smaller than their Ag(I)-based analogues$^{81,139,146,204}$ which shows a desirable value for photovoltaic applications. Then synthesis method 4 was attempted to prepare Cs$_2$CuInCl$_6$. Obviously, from PXRD patterns in Figure 4.5a, a by-product could be seen except for the targeted perovskite phase. Notably, this by-product is Cs$_2$InCl$_5$.H$_2$O which is the same one during the synthesis of Cs$_2$AgInCl$_6$ whereas here, the content of by-product is very high. Rietveld refinement has been employed to estimate the crystalline phase compositions of multiphase mixtures. Quantitative analysis result shows that the final product contains 43.6% of Cs$_2$CuInCl$_6$ and 56.4% of Cs$_2$InCl$_5$.H$_2$O.

Figure 4.5 PXRD pattern of impure Cs$_2$CuInCl$_6$ (a) and Rietveld refinement of impure Cs$_2$CuInCl$_6$ (b), ($R_{wp}$ (%)) = 14.01, $R_{exp}$ (%) = 13.03, GOF= 1.08)
Use DFT calculations, Xiao et al. explained that since the higher energy level of Cu 3d orbitals as compared to that of Ag 4d orbitals, and the ionic size of Cu(I) is smaller than Ag(I), Cu(I)-based halide compounds are more energetically favorable within 4- or 3-fold coordination, rather than 6-fold coordination. The product they prepared with solid state synthesis confirmed their predictions. No Cu(I)-based double perovskites formed under the conditions examined, rather, 4-fold coordinated CsCu$_2$Cl$_3$ together with Cs$_3$In$_2$Cl$_9$ appeared within the product. This is different from our product, in which about half of the content is the required double perovskite phase. In fact, the starting chemical CuCl would be unstable with respect to disproportionation into Cu and CuCl$_2$, it is predicted that the purity of Cs$_2$CuInCl$_6$ phase could be improved if the reaction is under a N$_2$ atmosphere.

4.2.3 Sb and Bi alloyed Cs$_2$NaInCl$_6$

4.2.3.1 Sb alloyed Cs$_2$NaInCl$_6$

When Sb was alloyed with Cs$_2$NaInCl$_6$, the materials showed blue emission under UV light which makes it a promising blue phosphor for applications in near-UV excitation. Here, a nominal Cs$_2$NaIn$_{0.9}$Sb$_{0.1}$Cl$_6$ composition was prepared. The accuracy of the In$^{3+}$:Sb$^{3+}$ compositional ratios in the final product was further confirmed using ICP-OES technique which yielded result of Cs$_2$NaIn$_{0.97}$Sb$_{0.03}$Cl$_6$. The lattice parameter extracted by Rietveld refinement is 10.5389(3) Å. The crystals of both Cs$_2$NaInCl$_6$ and Cs$_2$NaIn$_{0.97}$Sb$_{0.03}$Cl$_6$ were light yellow, exhibiting no absorption in the visible region, indicating a wide band gap which is due to parity-forbidden transitions.
As shown in Figure 4.6b, Cs₂NaIn₀.₉₇Sb₀.₀₃Cl₆ exhibits bright blue photoluminescence, centered at 445 nm with a photoluminescent quantum yield of 63% while Cs₂NaInCl₆ shows no appreciable PL. As introduced in Chapter 1, for ns² ions Sb³⁺, the ground state is denoted as ¹S₀, whereas the excited state splits into four energy levels, ¹P₁, ³P₀, ³P₁, and ³P₂. The ¹S₀→¹P₁ transition is allowed while the ¹S₀→³P₁ transition is partially allowed due to spin–orbit coupling. But for ¹S₀→³P₂ and ¹S₀→³P₀, the transitions are totally forbidden at the electric dipole transition level. Cs₂NaInCl₆ is a wide bandgap compound (Eg ≈ 5.1 eV). As soon as Sb³⁺ is incorporated, characteristic 5s²→5s¹p¹ absorption transitions of the [SbCl₆]³⁻ octahedra will appear, the blue emission can be ascribed to localized Sb³⁺ excited state relaxation via a ³P₁ → ¹S₀ pathway, similar to the case of Cs₂NaMCl₆ (M = Sc, Y, La) matrices. The magnitude of the Stokes shift is indicative of the extent of an excited state reorganization of the [SbCl₆]³⁻ octahedra.

4.2.3.2 Sb/Bi alloyed Cs₂NaInCl₆

Different from Sb, the Bi alloyed Cs₂NaInCl₆ materials do not show emission under UV light (Figure 4.7a). But according to the report from Zhou et al., under ultraviolet excitation, Sb³⁺/Bi³⁺ co-doped Cs₂NaInCl₆ double perovskites exhibit dual-emission consist of blue and yellow emission which cover the wavelength range 380–800 nm and thus show white light emission ultimately. They explained that the blue emission (center at 450 nm) originated from [SbCl₆]³⁻ octahedrons, and the PLE came from pseudo- Jahn Teller splitting of the ¹S₀ to ³P₁ transition. For the yellow emission (center at ~580 nm), it is actually not directly originated from [BiCl₆]³⁻ octahedrons. It is also caused by STEs in [SbCl₆]³⁻ octahedrons but was greatly enhanced by the Bi³⁺ dopant to increased lattice distortions.
However, the situation is different for our alloyed materials. A nominal alloyed compound 
Cs$_2$NaIn$_{0.9}$Sb$_{0.05}$Bi$_{0.05}$Cl$_6$ was prepared, it showed blue emission under UV light (Figure 4.7a) and had the same PL emission band with Cs$_2$NaIn$_{0.97}$Sb$_{0.03}$Cl$_6$ in Figure 4.8a which indicates that the additional Bi alloying didn’t change the physical property of Sb alloyed Cs$_2$NaInCl$_6$.

Interestingly, when additional nominal 10% Ag was alloyed as Cs$_2$Na$_{0.9}$Ag$_{0.1}$In$_{0.9}$Sb$_{0.1}$Cl$_6$, the PL spectrum showed a certain redshift. However, when more Ag was added, i.e. 50%, the product shows no emission. The possible reason is that Cs$_2$NaInCl$_6$ possess wide band gap, the VBM and CBM are mainly derived from the Cl 3p and In 5s orbitals, respectively, once Ag is alloyed, a strong p–d coupling between the Ag 4d and Cl 3p orbitals would happen which changed the relative contributions from Ag and Cl at the bands near the band gap. Thus, the CBM of the resulting alloyed compound is slightly shifted to lower energy level while the VBM are pushed to higher energy levels which cause a smaller band gap. As a result, PL spectrum of Cs$_2$Na$_{0.9}$Ag$_{0.1}$In$_{0.9}$Sb$_{0.1}$Cl$_6$ showed redshift. For the case of Cs$_2$Na$_{0.5}$Ag$_{0.5}$In$_{0.9}$Sb$_{0.1}$Cl$_6$, as soon as the Ag content increasing, the band gap continues decreasing, when the energy of $^1S_0 \rightarrow ^3P_1$
transition is approaching to the band edge, thermal excitation could be allowed into the conduction band and subsequent energy migration may happens.\textsuperscript{39} Notably, PL spectra of a nominal compound Cs\(_2\)Na\(_{0.5}\)Ag\(_{0.5}\)In\(_{0.9}\)Sb\(_{0.05}\)Bi\(_{0.05}\)Cl\(_6\) exhibited a broadband visible emission. Comparing with Cs\(_2\)Na\(_{0.5}\)Ag\(_{0.5}\)In\(_{0.9}\)Sb\(_{0.1}\)Cl\(_6\), it indicates that this broadband emission should be originated from STE induced by Bi. Regarding the Bi alloyed compositions, it has already been discussed in last chapter.

![Figure 4.8](image)

**Figure 4.8** (a) Emission spectra of Cs\(_2\)NaIn\(_{0.97}\)Sb\(_{0.03}\)Cl\(_6\), nominal alloyed materials Cs\(_2\)NaIn\(_{0.9}\)Sb\(_{0.05}\)Bi\(_{0.05}\)Cl\(_6\), Cs\(_2\)Na\(_{0.9}\)Ag\(_{0.1}\)In\(_{0.9}\)Sb\(_{0.1}\)Cl\(_6\) and (b) Cs\(_2\)Na\(_{0.5}\)Ag\(_{0.5}\)In\(_{0.9}\)Sb\(_{0.1}\)Cl\(_6\).

### 4.2.4 Cs\(_2\)InCl\(_5\).H\(_2\)O and Sb alloyed Cs\(_2\)InCl\(_5\).H\(_2\)O

As we mentioned before, impurity compound Cs\(_2\)InCl\(_5\).H\(_2\)O existed when Cs\(_2\)AgInCl\(_6\) powder was synthesized. More works were conducted on further studying this material. Pure Cs\(_2\)InCl\(_5\).H\(_2\)O is very easy to synthesize with synthesis method 2 by only adding stoichiometric In\(_2\)O\(_3\) and CsCl. The obtained Cs\(_2\)InCl\(_5\).H\(_2\)O is colorless transparent crystal belongs to the space group Pnma [cell parameters: \(a = 14.4215(9)\) Å, \(b = 10.3872(8)\) Å, \(c = 7.4150(6)\) Å] which was confirmed by XRD analysis, in agreement with previous report\textsuperscript{25}. In this structure, each Indium atom is coordinated with five Cl atoms and one O atom from coordinating water to form an \([\text{InCl}_5(\text{H}_2\text{O})]\)\(^2-\) octahedron. Every \([\text{InCl}_5(\text{H}_2\text{O})]\)\(^2-\) octahedron is separated by Cs\(^+\) ions to create a “0D” structure, similar to the A\(_2\)B(IV)X\(_6\) perovskite\textsuperscript{25,208}.

![Diagram](image)
A nominal Cs$_2$In$_{0.99}$Sb$_{0.01}$Cl$_5$.H$_2$O composition was prepared with the same synthesis procedure. And ICP measurements give the accurate composition as Cs$_2$In$_{0.99}$Sb$_{0.01}$Cl$_5$.H$_2$O. It shows that there is no emission for Cs$_2$InCl$_5$.H$_2$O under UV light while the Sb alloyed Cs$_2$InCl$_5$.H$_2$O show yellow light (Figure 4.10a). The PL spectrum of Cs$_2$In$_{0.99}$Sb$_{0.01}$Cl$_5$.H$_2$O displayed a broad emission from 480 to 850 nm with an emission peak centered at 610 nm which can be ascribed to the $^3P_1\rightarrow^1S_0$ transition. And as shown in Figure 4.10b, lifetime of Cs$_2$In$_{0.99}$Sb$_{0.01}$Cl$_5$.H$_2$O is much longer than Cs$_2$InCl$_5$.H$_2$O and has characteristic lifetimes on microsecond scale (Figure 4.10c) which are typical features of STE emission. In addition, it is also shown that, the lifetimes of Cs$_2$In$_{0.99}$Sb$_{0.01}$Cl$_5$.H$_2$O is longer than that of Cs$_2$In$_{0.97}$Sb$_{0.03}$Cl$_6$, which indicated that localization of Cs$_2$In$_{0.99}$Sb$_{0.01}$Cl$_5$.H$_2$O is stronger caused by larger lattice deformation which are consistent with its large Stoke shift.

Figure 4.9 (a), Photo of Cs$_2$InCl$_5$.H$_2$O crystal. (b), Crystal structure of Cs$_2$InCl$_5$.H$_2$O. (c), Rietveld refinement of Cs$_2$InCl$_5$.H$_2$O, $R_{wp}$ (%) = 10.80, and GOF = 0.17. (d), Rietveld refinement of Cs$_2$(In$_{0.99}$Sb$_{0.01}$)Cl$_5$.H$_2$O, $R_{wp}$ (%) = 10.96, and GOF = 0.17.

Figure 4.10 (a), Emission spectra of Cs$_2$InCl$_5$.H$_2$O and Cs$_2$In$_{0.99}$Sb$_{0.01}$Cl$_5$.H$_2$O at excitation wavelength 356nm (insert photo is Cs$_2$InCl$_5$.H$_2$O and Cs$_2$In$_{0.99}$Sb$_{0.01}$Cl$_5$.H$_2$O samples under UV light). (b), PL lifetime of Cs$_2$InCl$_5$.H$_2$O and Cs$_2$In$_{0.99}$Sb$_{0.01}$Cl$_5$.H$_2$O. (c), PL lifetime of Cs$_2$In$_{0.99}$Sb$_{0.01}$Cl$_5$.H$_2$O and Cs$_2$In$_{0.97}$Sb$_{0.03}$Cl$_6$.
4.2.5 Cs\(_3\)InCl\(_6\) and Sb alloyed Cs\(_3\)InCl\(_6\)

Recently, Woodward’s group explored a synthetic route to remove the H\(_2\)O molecules in Rb\(_2\)InCl\(_5\)·H\(_2\)O and obtain another 0D material Rb\(_3\)InCl\(_6\) using nonaqueous organic solvents (e.g. acetonitrile).\(^41\) Here, Cs\(_3\)InCl\(_6\) and Cs\(_3\)In\(_{0.99}\)Sb\(_{0.01}\)Cl\(_6\) were prepared through the same strategy. Specifically, add 1 mmol of Cs\(_2\)InCl\(_5\)·H\(_2\)O (or Cs\(_2\)In\(_{0.99}\)Sb\(_{0.01}\)Cl\(_5\)·H\(_2\)O) crystal to 20 mL of acetonitrile and sonicating the mixture. The resulting white powder was filtered and washed with acetonitrile to acquire Cs\(_3\)InCl\(_6\) (or Cs\(_3\)In\(_{0.99}\)Sb\(_{0.01}\)Cl\(_6\)). Cs\(_3\)InCl\(_6\) has no emission under UV light while Cs\(_3\)In\(_{0.99}\)Sb\(_{0.01}\)Cl\(_6\) shows blue-green. As observed in Figure 4.11a, Cs\(_3\)In\(_{0.99}\)Sb\(_{0.01}\)Cl\(_6\) exhibits photoluminescence centered ~515 nm with a PLQY as high as 96% originating from the \(^3\)P\(_1\)→\(^1\)S\(_0\) transition of Sb\(^{3+}\). In Figure 4.11b, the conversion from Sb alloyed hydrate phase to Cs\(_3\)In\(_{0.99}\)Sb\(_{0.01}\)Cl\(_6\) through sonication in acetonitrile was monitored by following the change of PL color from yellow to blue-green under UV excitation.

![Figure 4.11](image)

Figure 4.11 (a) Emission spectra of Cs\(_3\)InCl\(_6\) and Cs\(_3\)In\(_{0.99}\)Sb\(_{0.01}\)Cl\(_6\) at excitation wavelength 356nm. (b) Photoluminescence under UV light, schematic diagram of synthetic route from Cs\(_2\)In\(_{0.99}\)Sb\(_{0.01}\)Cl\(_5\)·H\(_2\)O to Cs\(_3\)In\(_{0.99}\)Sb\(_{0.01}\)Cl\(_6\) by sonication in acetonitrile.

From PXRD pattern in Figure 4.12a, the obtained Cs\(_3\)InCl\(_6\) was not pure since a small amount of residual Cs\(_2\)InCl\(_5\)·H\(_2\)O still exist. But for Cs\(_3\)In\(_{0.99}\)Sb\(_{0.01}\)Cl\(_6\), PXRD pattern in Figure 4.12b confirmed it as a pure crystalline compound. Majher et al. compared Rietveld refinement of Rb\(_3\)InCl\(_6\) with the C2/c structure (R\(_{wp}\) = 7.958%) vs the P21/a structure (R\(_{wp}\) = 10.949%),
confirming the C2/c solution with the unit cell dimensions of $a = 25.449(2) \text{ Å}$, $b = 7.7836(5) \text{ Å}$, $c = 12.5571(9) \text{ Å}$, $\alpha = 90^\circ$, $\beta = 99.771(2)^\circ$, $\gamma = 90^\circ$.\(^{41}\) Zhu et al. prepared nanocrystal for $\text{Rb}_3\text{InCl}_6$, and the XRD pattern of $\text{Rb}_3\text{InCl}_6$ nanocrystals have a good match with the monoclinic $\text{Rb}_3\text{TlCl}_6$ structure (ICSD no. 300228) belonging to the P121/c1 space group.\(^{206}\) Herein, using the $\text{Cs}_3\text{BiCl}_6$ structure (COD ID: 1004082) as a starting model, I performed a Rietveld refinement for the $\text{Cs}_3\text{In}_{0.99}\text{Sb}_{0.01}\text{Cl}_6$ PXRD data which gave a good fit, $R_{wp}=7.98\%$, with the C2/c structure, in agreement with the work of Majher. The 1 mol % Sb alloying should not significantly change the crystal structure of the $\text{Cs}_3\text{InCl}_6$ and the unit cell dimensions, on one hand, the alloyed content of Sb is very low, on the other hand, Sb\(^{3+}\) cations have similar ionic radii to In\(^{3+}\) cations (80 pm for In\(^{3+}\) and 76 pm for Sb\(^{3+}\)). Therefore, here the crystal data of $\text{Cs}_3\text{In}_{0.99}\text{Sb}_{0.01}\text{Cl}_6$ in Table 4.1 was used as a reference to study $\text{Cs}_3\text{InCl}_6$. The unit cell dimensions value of $\text{Cs}_3\text{In}_{0.99}\text{Sb}_{0.01}\text{Cl}_6$ is larger than that of reported $\text{Rb}_3\text{InCl}_6$, that is because the ionic radii of Cs\(^+\) is larger than that of Rb\(^+\).

### Table 4.1. Crystal data and structure refinement for $\text{Cs}_3\text{In}_{0.99}\text{Sb}_{0.01}\text{Cl}_6$.

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>$\text{Cs}<em>3\text{In}</em>{0.99}\text{Sb}_{0.01}\text{Cl}_6$</th>
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<tr>
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<tr>
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<td>$b=8.0445(6)\text{ Å}$</td>
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<tr>
<td></td>
<td>$c=12.887(1)\text{ Å}$</td>
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<tr>
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<tr>
<td></td>
<td>$\gamma=90^\circ$</td>
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![Graph (a)](image1.png)

![Graph (b)](image2.png)
Figure 4.12 XRD patterns of Cs$_3$InCl$_6$ (a) and Cs$_3$In$_{0.99}$Sb$_{0.01}$Cl$_6$ (b). Rietveld refinement of Cs$_3$In$_{0.99}$Sb$_{0.01}$Cl$_6$, $R_{wp}$ (%) = 7.98, and GOF = 0.15 (c) (insert graph is monoclinic structure unit cell of Cs$_3$In$_{0.99}$Sb$_{0.01}$Cl$_6$)

4.2.6 Comparison of Sb alloyed Cs$_2$NaInCl$_6$, Cs$_2$InCl$_5$.H$_2$O and Cs$_3$InCl$_6$

To provide insights into the electronic structure of Sb alloyed materials, Cs$_2$NaIn$_{0.97}$Sb$_{0.03}$Cl$_6$, Cs$_3$In$_{0.99}$Sb$_{0.01}$Cl$_6$ and Cs$_2$In$_{0.99}$Sb$_{0.01}$Cl$_5$.H$_2$O, a comparison for the PL spectra of them was shown in Figure 4.13a. As observed, from Cs$_2$NaIn$_{0.97}$Sb$_{0.03}$Cl$_6$ to Cs$_3$In$_{0.99}$Sb$_{0.01}$Cl$_6$ and then to Cs$_2$In$_{0.99}$Sb$_{0.01}$Cl$_5$.H$_2$O, both the Stoke shift of the emission band and the FWHM keeps growing larger. In principle, Sb-doped materials are all characterized by identical near-UV absorption features that have been attributed to electronic transitions within the [SbCl$_6$]$^{3-}$ octahedra, which are considered as sensitizers in a host matrix that is transparent to light at the band edges (due to parity-forbidden transitions).$^{24,25,39,41,186,205–207}$ In the structural dimensionality 0D, or in 3D crystal structure but surrounded by six wide bandgap octahedra such as [NaCl$_6$]$^5^-$, the [SbCl$_6$]$^{3-}$ octahedra is considered as electronically isolated and the absorption from which could be described as an atomic-like excitation influenced by spin–orbit coupling. Normally, at high energies it features two absorption peaks, a broad absorption centred $\sim$260 nm is ascribed to the spin-allowed $^1S_0 \rightarrow ^1P_1$ transition (C band) while a weak peak at $\sim$280 nm is assigned to the spin and parity forbidden $^1S_0 \rightarrow ^3P_2$ transition (B band) which appears because vibronic coupling and spin-orbit coupling relax the selection rules. At lower energies, a characteristic double-absorption in the 300–400 nm range can be assigned to spin forbidden, parity allowed $^5S_0 \rightarrow ^3P_1$ transition (A band).$^{39,41,70,205,206,209}$ This transition is split into two peaks which is ascribed to a dynamic Jahn–Teller distortion of excited state induced by electron–phonon (vibronic) coupling.$^{39,41,120,186}$

In emission, the [SbCl$_6$]$^{3-}$ octahedra also act as recombination centres in host by undergoing a structural reorganization of the excited state which accounts for the Stokes shift. However,
as shown in Figure 4.13a, the shift varies when the host is different. This variability has been attributed to the different coordination environments probed by the Sb\(^{3+}\) cations, i.e. [SbCl\(_6\)]\(^{3-}\) or [SbCl\(_5\)(H\(_2\)O)]\(^{2-}\) octahedra. Compared to the more symmetric Cs\(_2\)NaInCl\(_6\), the octahedral tilting distortion of Cs\(_3\)InCl\(_6\) (Figure 4.13c) may enhance the electronic isolation of the In/Sb-centred octahedra which facilitate electron and hole localization on Sb\(^{3+}\) sites, leading to high efficiency photoluminescence (near-unity). In addition, the distorted crystal structure induced electron–phonon interaction and resulted in a larger Stokes shift and FWHM.

![Figure 4.13](image)

Figure 4.13 (a) Emission spectra of Cs\(_2\)NaIn\(_{0.97}\)Sb\(_{0.03}\)Cl\(_6\), Cs\(_3\)In\(_{0.99}\)Sb\(_{0.01}\)Cl\(_6\) and Cs\(_2\)In\(_{0.99}\)Sb\(_{0.01}\)Cl\(_5\).H\(_2\)O at excitation wavelength 356nm (black arrows indicate the FWHM). (b) Crystal structure sketch of Cs\(_2\)NaInCl\(_6\) (here the octahedra for NaCl\(_6\) was not shown to emphasize that the [InCl\(_6\)]\(^{3+}\) octahedron is electronically isolated\(^{67}\)) (b) Cs\(_3\)InCl\(_6\), and (c) Cs\(_2\)InCl\(_5\).H\(_2\)O. The Cs\(^+\) ions are shown in cyan, Na\(^+\) in yellow, In\(^{3+}\) in pink, O\(^2-\) in red, and Cl\(^-\) in green.

When Sb doped in host material Cs\(_3\)InCl\(_6\), activator Sb\(^{3+}\) coordinates by six same Cl\(^-\) ions, thus [SbCl\(_6\)]\(^{3-}\) is a regular octahedron (Figure 4.14, left).\(^{207}\) However, for Sb doped Cs\(_2\)InCl\(_5\).H\(_2\)O, [SbCl\(_5\)(H\(_2\)O)]\(^{2-}\) consists of five chlorine anions and one crystalline water molecule, forming a asymmetric coordination environment (Figure 4.14, right) and subsequently producing a more pronounced structural distortion in the excited state. In other words, by analysing coordination environment in these three host materials, it is found that the greater degree of Jahn–Teller distortion, the more red-shifted of the STEs emission and the longer the STEs
lifetime. Thus, for in 0D perovskites, it may be an effective way to tune the PL emission color by controlling the distortion of octahedron.

Figure 4.14 The transformation between a regular octahedron $[\text{SbCl}_6]^-$ and a asymmetric $[\text{SbCl}_5(\text{H}_2\text{O})]^-$ octahedra.\textsuperscript{207}

4.2.7 $\text{Cs}_2\text{AgBiX}_6$ and the A-site organic cation analogue

4.2.7.1 $\text{Cs}_2\text{AgBiBr}_6$

The Bi/Ag based double perovskites have drawn a remarkable interest since a number of studies introduced $\text{Cs}_2\text{AgBiBr}_6$, which exhibit band gaps in the visible and the photoluminescence (PL) lifetime of several hundred nanoseconds and calculated charge carrier effective masses close to those calculated for $\text{MAPbI}_3$.\textsuperscript{92} Although the gaps of these Bi-based double perovskites are indirect, which is not ideal for thin film photovoltaic applications, strikingly, they are showing the promising potential application as the absorber material\textsuperscript{7,29–31} and photodetectors\textsuperscript{94,144,210} which is a newly popular field for lead-free double perovskite with indirect bandgaps.

The synthesis of $\text{Cs}_2\text{AgBiBr}_6$ was prepared with synthesis method 1 and the crystals were much duller red. After grinding, the sample become luminescent orange powder as shown in Figure 4.15.

Figure 4.15 Photos of synthesized $\text{Cs}_2\text{AgBiBr}_6$ crystal, (insert photos are grinded powder)

The Rietveld refinement fits to the PXRD patterns of $\text{Cs}_2\text{AgBiBr}_6$ are shown in Figure 4.16a. Both compounds adopt the cubic double perovskite structure with $\text{Fm} \bar{3} \text{m}$ space group symmetry. The lattice parameters extracted from the refinements of $\text{Cs}_2\text{AgBiBr}_6$ are
11.2750(5) Å and the band gaps extracted by Tauc plot is 2.07 eV. These values are all consistent with other reports.

![Graph of Cs₂AgBiBr₆ Rietveld refinement and Tauc plot](image)

**Figure 4.16** (a), Rietveld refinement of Cs₂AgBiBr₆, Rwp (%) = 12.66, and GOF = 0.14. (b), Tauc plot of Cs₂AgBiBr₆.

### 4.2.7.2 Band gap engineering of Cs₂AgIn₁₋ₓBiₓBr₆

Because of its indirect band gap property, Cs₂AgBiBr₆ almost rules out any potential photovoltaic and lighting applications, but their In-based counterparts exhibit direct band gap. So, a general design strategy is presented for tuning the convergence of direct and indirect band gaps based on trivalent metals adjustment, that is Cs₂AgIn₁₋ₓBiₓBr₆.

Synthesis method 1 was employed to prepare the alloyed double perovskite Cs₂AgIn₁₋ₓBiₓBr₆. I firstly start from adding Indium to Cs₂AgBiBr₆, and prepared Cs₂AgIn₀.₁Bi₀.₉Br₆ and Cs₂AgIn₀.₂Bi₀.₈Br₆. As shown in Figure 4.17, the color of the alloyed double perovskite powders changed from luminescent orange to persimmon. And the peak shifted to higher angles of PXRD pattern when Indium content was increasing confirmed the alloyed compositions (Figure 4.18a). It is because the ionic radii of In³⁺ (0.8 Å) is smaller than Bi³⁺ (1.03 Å) which caused lattice parameter of Indium alloyed double perovskite reduce. In addition, the band gap of Indium alloyed materials increased since Cs₂AgInBr₆ has larger band gap than Cs₂AgBiBr₆ (Figure 4.18b).

![Photos of Cs₂AgIn₁₋ₓBiₓBr₆ materials](image)

**Figure 4.17** Photos of Cs₂AgIn₁₋ₓBiₓBr₆ materials

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One reference\(^86\) reported pure alloyed Cs\(_2\)AgIn\(_{1-x}\)Bi\(_x\)Br\(_6\) (x=0.25, 0.5, 0.75) were prepared with solid state synthesis. However, with my method, if more Indium was added, for compound Cs\(_2\)AgIn\(_{0.5}\)Bi\(_{0.5}\)Br\(_6\), two separated phases appeared in the product which are mixture of orange crystal and yellow crystal. The orange crystal is assumed to be Cs\(_2\)AgBiBr\(_6\), and the composition of yellow crystal is revealed when Cs\(_2\)AgIn\(_{0.9}\)Bi\(_{0.1}\)Br\(_6\) was synthesized. As shown in Figure 4.18c, PXRD pattern of Cs\(_2\)AgIn\(_{0.9}\)Bi\(_{0.1}\)Br\(_6\) fits well with Cs\(_2\)InBr\(_5\).H\(_2\)O which indicate that this method is not suitable to obtain alloyed double perovskite Cs\(_2\)AgIn\(_{1-x}\)Bi\(_x\)Br\(_6\) when Indium content is high.

4.2.7.3 Cs\(_2\)AgBiI\(_6\) and MA\(_2\)AgBiI\(_6\)

Iodide double perovskites Cs\(_2\)AgBiI\(_6\) are highly desirable since their band gaps are expected to be similar to those found in the lead iodides perovskite, however the synthesis of iodides appears to have been a challenge because of the negative decomposition energy (Cs\(_2\)AgBiI\(_6\) → 1/2CsAgI\(_3\) + 1/2Cs\(_3\)Bi\(_2\)I\(_9\)).\(^{198,199}\) Cheng et al. reported ((CH\(_3\)NH\(_3\))\(_2\)AgBiI\(_6\)) which was
synthesized through solid-state reaction. MA\textsubscript{2}AgBi\textsubscript{6} (MA is the abbreviation used to denote the methylammonium cation) was tried to prepare following the same method with synthesis method 3 and dull red powder samples were obtained. According to XRD pattern in Figure 4.19a, we can found that the acquired compound fit well with MA\textsubscript{3}Bi\textsubscript{2}I\textsubscript{9} which belongs to space group P6\textsubscript{3}/mmc.\textsuperscript{211–215} Thus, it is speculated that the main ingredient in the product is MA\textsubscript{3}Bi\textsubscript{2}I\textsubscript{9} but not MA\textsubscript{2}AgBi\textsubscript{6}. Instead of corner-sharing in [MX\textsubscript{6}]\textsuperscript{4−}octahedra in AMX\textsubscript{3}, Figure 4.19b showed that the [Bi\textsubscript{6}]\textsuperscript{3+} octahedra in MA\textsubscript{3}Bi\textsubscript{2}I\textsubscript{9} crystal are linked by face-sharing.\textsuperscript{211}

![Figure 4.19 (a), PXRD pattern of synthesized MA\textsubscript{2}AgBi\textsubscript{6} (insert photos are powder sample of MA\textsubscript{2}AgBi\textsubscript{6} prepared by solid state synthesis). (b), Crystal structure of MA\textsubscript{3}Bi\textsubscript{2}I\textsubscript{9}.

As we discussed before, Cs\textsubscript{2}AgBi\textsubscript{6} phase is not stable in bulk form (single crystals or thin films), but Yang et al. reported that Cs\textsubscript{2}AgBi\textsubscript{6} could be stable in nanostructures.\textsuperscript{216} Creutz et al. reported the synthesis of colloidal nanocrystals of Cs\textsubscript{2}AgBi\textsubscript{6} by anion-exchange method using trimethylsilyl iodide.\textsuperscript{148} This could be a feasible way for further understanding the physical property for unstable compound like Cs\textsubscript{2}AgBi\textsubscript{6}.

### 4.3 Conclusion

Double perovskites exhibit extended three-dimensional structures resembling ABX\textsubscript{3} perovskites while permitting a wide variety of cations to be incorporated into the octahedrally coordinated B\textsuperscript{+}/B\textsuperscript{3+} site enables access to a potentially large number of alternative compositions and electronic structures. Thus, in this chapter, I try to exploit the versatile applications of novel lead-free metal halide perovskite materials.
Cs₂AgInBr₆ was very hard to be synthesized since the phase Cs₂InBr₅.H₂O was favourable instead of phase Cs₂AgInBr₆. Meanwhile, according to the report, Cs₂AgInBr₆ degrades very quickly under light illumination which is a significant challenge for application in photovoltaics. Interestingly, it is reported that Cs₂InBr₅.H₂O enables a bright red PL emission under UV light while its dehydrated form emits a bright yellow PL emission under UV light which could be an excellent material applied in fields such as water-/temperature-sensing, photodetection, and the development of light-emitting devices.²⁰² MA₂AgInBr₆ belongs to the trigonal system and has a space group P 3 m1, it’s not a suitable material used in optoelectronic field. Cs₂CuInCl₆ was synthesized but with a large amount of second phase Cs₂InCl₅.H₂O. It seems that purer Cs₂CuInCl₆ could be obtained if the synthesis condition is improved.

MA₂AgBiI₆ was attempted to synthesize, however the final product was recognized as MA₃Bi₂I₉.

More interestingly, Cs₂NaInCl₆, Cs₂InCl₅.H₂O and Cs₃InCl₆ all show no emission under UV light while the Sb alloyed Cs₂NaInCl₆, Cs₂InCl₅.H₂O and Cs₃InCl₆ exhibit blue emission, yellow emission, and blue-green emission under UV light respectively. They are all promising materials for light-emitting diodes (LEDs). And the understanding of luminescence mechanism in ns² ion activated halide perovskite will help the search and the design of more efficient phosphors.
CHAPTER 5 Conclusion and future work

For double perovskites $A_2B^+B^{3+}X_6$, there is more flexibility to engineer the electronic band since all the cations $A^+$, $B^+$, $B^{3+}$ and anions $X^-$ may be substituted while the structure remains.\textsuperscript{26,66,87,217} Specially, the tunability of $B^+/B^{3+}$ and the related $[BX_6]$ octahedron can effectively tailor and change the band gap, parity symmetry, direct vs indirect nature.\textsuperscript{218} This rich combinatorial chemistry leads to tunable optoelectronic properties and thus a great potential for a broad range of optoelectronic/electronic applications.

Single-component white light emitting materials $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{In}_{1-y}\text{Bi}_y\text{Cl}_6$ were introduced, the highest photoluminescence quantum yield (PLQY) of which is close to unity. To learn the mechanism for this high efficiency, we can started from $\text{Cs}_2\text{AgInCl}_6$. It exhibits broad emission (400-800 nm) however, the PLQY is extremely low. The VBM is mainly derived from $\text{Ag} 4d/\text{Cl} 3p$ orbitals which is very flat, whereas the CBM is mainly derived from delocalized $\text{In} 5s$ states, indicating the wave function of holes is strongly confined at $[\text{AgCl}_6]$ octahedral. After excitation, holes are quickly trapped at $[\text{AgCl}_6]$ octahedra and change the electronic configuration of silver from $4d^{10}$ to $4d^9$, causing a strong Jahn–Teller distortion of $[\text{AgCl}_6]$ octahedron.\textsuperscript{23} Although the hole wave function of the STE in $\text{Cs}_2\text{AgInCl}_6$ is localized, the electron wave function is rather spread, leading to the small overlap between hole wave function and electron wave function. The Na cations contribute to neither conduction band minimum (CBM) nor valence band maximum (VBM) of the alloy, they serve as quantum wells to confine the spatial distribution of the STE, especially the electron wave function, enhancing radiative recombination. Meanwhile, Bi doping could create a shallow new state above VBM, thus, optical excitations are captured by the presence of this new state instead of being trapped by defects, producing bright excitons which are already present in the no Bi doped compound. Obviously, such outstanding emission properties are due to the simultaneous presence of Bi and Silver. However, the exact mechanism for this high efficiency is still under investigation.

The $ns^2$ electronic configuration of the metal ions ($\text{Sb}^{3+}$ and $\text{Bi}^{3+}$) doping in $\text{Cs}_2\text{AgInCl}_6$ and $\text{Cs}_2\text{NaInCl}_6$ has led to a remarkable change in both their optical absorption and emission properties. Compounds like $\text{Sb}^{3+}$ doped $\text{Cs}_2\text{NaInCl}_6$ have emerged as intense blue light emitting phosphors. Furthermore, some 0D perovskite materials originate from second phase
of double perovskite synthesis were also studied, e.g. $\text{Cs}_2\text{InCl}_5\cdot\text{H}_2\text{O}$ and $\text{Cs}_2\text{InBr}_5\cdot\text{H}_2\text{O}$. Sb alloyed materials $\text{Cs}_2\text{NaIn}_{0.97}\text{Sb}_{0.03}\text{Cl}_6$, $\text{Cs}_3\text{In}_{0.99}\text{Sb}_{0.01}\text{Cl}_6$ and $\text{Cs}_2\text{In}_{0.99}\text{Sb}_{0.01}\text{Cl}_6\cdot\text{H}_2\text{O}$, were compared, different from the more symmetric $\text{Cs}_2\text{NaInCl}_6$, the octahedral tilting distortion of $\text{Cs}_3\text{InCl}_6$ may enhance the electronic isolation of the In/Sb-centred octahedra which facilitate electron and hole localization on Sb$^{3+}$ sites, leading to high efficiency photoluminescence (near-unity) of blue-green while a asymmetric coordination environment in $[\text{SbCl}_5(\text{H}_2\text{O})]^2-$ producing a more pronounced structural distortion in the excited state result in yellow emission with larger red-shift.

For the future, the role of Ag and Bi will be further investigated by ultrafast spectroscopy to understand what exactly makes the compound to achieve near-unity photoluminescence. In addition, the synthesis techniques may also lead different PLQY for same composition because they affect the surface traps and defects. Thus, I am interested in understanding the microstructure in the lattice next step since it is well known that disordered antisites are attributed to deep-level defects.\(^{219}\) Furthermore, films of these double perovskites are important for applications in devices but are not easy to be prepared by solution processing method. Thermal evaporation can be a possible deposition technique to make thin films and devices in the following work and to improve the potential of these materials as solid-state lighting and extend more applications.
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Figure A1 Rietveld refinements of crystal samples $\text{Cs}_2\text{AgIn}_{1-y}\text{Bi}_y\text{Cl}_6$, $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{InCl}_6$, $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{In}_{0.99}\text{Bi}_{0.01}\text{Cl}_6$, $\text{Cs}_2\text{NaIn}_{1-y}\text{Bi}_y\text{Cl}_6$ and $\text{Cs}_2\text{Na}_{0.99}\text{Ag}_{0.01}\text{In}_{1-y}\text{Bi}_y\text{Cl}_6$. The lattice parameters are compiled in the Table 3.3.
Figure A2 Rietveld refinements of powder samples \( \text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{InCl}_6 \) and \( \text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{In}_{0.99}\text{Bi}_{0.01}\text{Cl}_6 \). The lattice parameters are compiled in the Table 3.4.

Figure A3 Comparison of (220) peak for crystal and powder with same compositions.