

**Phase Transition, Doping (Mn^{2+} and Mo^{3+}) and
Luminescence of $\text{Cs}_2\text{NaBiCl}_6$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$
Perovskites: Bulk and Nanocrystals**

बिद्या बचस्पति की उपाधि की अपेक्षाओं की आंशिक पूर्ति में प्रस्तुत शोध प्रबंध

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***This thesis is dedicated to
My parents, Mr. Swapan Kumar Banerjee, Mrs. Jonaki Banerjee,
my sister, Ms. Sriparna Banerjee
without whom none of my success would be possible.***

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I certify that the work incorporated in the thesis entitled as, **“Phase Transition, Doping (Mn^{2+} and Mo^{3+}) and Luminescence of $\text{Cs}_2\text{NaBiCl}_6$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Perovskites: Bulk and Nanocrystals”** submitted by **Ms. Srijita Banerjee**, was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other university or institute.

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List of Abbreviations

0D: Zero-dimensional

1D: One-dimensional

2D: Two-dimensional

3D: Three-dimensional

CBM: Conduction band minima

DMF: Dimethyl formamide

DMSO: Dimethyl sulfoxide

DOS: Density of states

EPR: Electron paramagnetic resonance

FA: Formamidinium

FWHM: Full width at half maxima

HRTEM: High-resolution transmission electron microscopy

ICP-AES: Inductively coupled plasma atomic emission spectroscopy

ICP-MS: Inductively coupled plasma mass spectroscopy

LARP: Ligand-Assisted reprecipitation

MA: Methylammonium

NCs: Nanocrystals

NIR: Near-infrared

NMR: Nuclear magnetic resonance

pc-LED: Phosphor converted light emitting diode

PL: Photoluminescence

PLE: Photoluminescence excitation

rpm: Revolution per minute

STE: Self trapped exciton

List of Abbreviations

SWIR: Short wave infrared

TMSCL: Trimethylsilyl chloride

T-S: Tanabe -Sugano

UV: Ultraviolet

VBM: Valence band maxima

XRD: X-ray diffraction

Halide perovskites, particularly hybrid lead halide perovskites have recently emerged as an important class of semiconductors with properties related to solar cell, light emitting diodes (LED), chiral optoelectronics and so. Subsequently, a good amount of work has been reported developing Pb-free halide perovskites, though with a limited success in optoelectronic properties. Doping different transition metal ions and lanthanide ions in Pb-free halide double perovskites show interesting light emission properties suitable for phosphor converted LED applications in the visible and near-infrared region. Some of these double perovskites shows temperature dependent structural phase transition. The major emphasis of this thesis is to explore how the transition metal dopants or nanocrystalline size influence the structural phase transition of halide double perovskites, and tailor their light emission properties. The Chapter-wise content of the thesis work is discussed below.

Chapter 1: Introduction

This chapter introduces the fundamentals about the solid-to-solid phase transition in crystals with some well-known examples. A brief discussion about how the structural phase transition controls fundamental properties like optoelectronic, magnetic and dielectric, is provided. The structure-property correlations have been mainly discussed in the context of halide perovskites, which is the material class for the present thesis work. For example, band gap and light emission properties of MAPbBr₃ (MA: methylammonium) and CsPbI₃ can be tuned by changing the crystal structure from cubic to orthorhombic to tetrahedral. Besides, the effects of nanocrystal size shape on the optoelectronic properties have been discussed. All-inorganic Pb-free halide double perovskites have been introduced. Some of these double perovskites are not good emitters but are good choices for doping with different metal ions with different oxidation sites. The possible influences of lattice doping on structural phase transition and optical properties have been discussed, which led to defining the scope of the present thesis work.

Chapter 2A: Unveiling Temperature-Induced Structural Phase Transition and Luminescence in Mn²⁺-Doped Cs₂NaBiCl₆ Double Perovskite

Three dimensional all inorganic halide perovskites (ABX₃) often undergo structural phase transition upon change of external conditions like temperature and pressure. Cs₂NaBiCl₆ is one of the examples of halide double perovskites (A₂BB'X₆)

undergoing structural transition from cubic to tetragonal, below 110 K. At room temperature, $\text{Cs}_2\text{NaBiCl}_6$ does not emit light. Interestingly, Mn^{2+} doping yield orange-red (600 nm) light emission, upon exciting the host. Thus, using Mn^{2+} emission we can probe whether the emission is affected by the temperature-dependent structural phase transition of the $\text{Cs}_2\text{NaBiCl}_6$ host. The temperature-dependent (7 – 300 K) photoluminescence measurements show that nature of Mn^{2+} emission does not change due to structural phase transition. Similarly, electron paramagnetic data also do not get affected by the structural phase transition. But temperature-dependent (12 – 300 K) powder X-ray diffraction data of Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ clearly show the cubic to tetragonal phase transition below 110 K, similar to the undoped counterpart. These results suggest that in spite of the global structural change of the host, the local structure around the Mn^{2+} dopants do not change enough, providing a stable luminescence property over a wide range of temperatures.

Chapter 2B: Temperature-Dependent Phase Transition and Near-infrared Emission of Mo^{3+} -Doped $\text{Cs}_2\text{NaBiCl}_6$ Double Perovskite

We doped Mo^{3+} in the same host $\text{Cs}_2\text{NaBiCl}_6$, which undergoes a phase transition from cubic to tetragonal below 110 K. Mo^{3+} with $4d^3$ electron in an octahedral field shows intra-configurational spin-flip transition emitting ultra-narrow (FWHM ~ 11 meV) near-infrared (~1095 nm) emission. This sharp emission of Mo^{3+} is more sensitive to the local structure compared to the broad emission of Mn^{2+} discussed in Chapter 2A. Consequently, Mo^{3+} show a different trend in the emission peak energy, above and below the structural phase transition temperature ~110 K.

Chapter 3: Temperature Dependent Phase Transition in $\text{Cs}_2\text{NaBiCl}_6$ Nanocrystals: Size Effect

Bulk form of $\text{Cs}_2\text{NaBiCl}_6$ double perovskite undergoes a structural phase transition at ~ 110 K, as discussed in Chapter-2. Does the same phase transition occur for their nanocrystals as well? To answer this question, we prepared colloidal $\text{Cs}_2\text{NaBiCl}_6$, with edge length 12 nm. Then, temperature-dependent powder X-ray diffraction and Raman spectroscopy was used to probe the possibility of structural phase transition $\text{Cs}_2\text{NaBiCl}_6$ nanocrystals. At room temperature, $\text{Cs}_2\text{NaBiCl}_6$ nanocrystals crystallize in the cubic structure, similar to the micrometer sized bulk

samples. However, we did not find any signature of phase transition at lower temperatures at lower temperatures till ~ 12 K, in clear difference to their bulk counterpart. This difference, the absence of phase transition, probably arise from the high surface-to-volume ratio of nanocrystals. The surface defects along with the capping ligand contributions significantly alters the surface energy of nanocrystals, and probably this large contribution of surface energy stabilizes the unusual cubic phase at lower temperatures as well.

Chapter 4: High-Temperature Synthesis of Colloidal $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Perovskite Nanoplatelets and Nanocubes

Nanocrystals of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ or MAPbBr_3 ($\text{MA} = \text{CH}_3\text{NH}_3^+$) perovskite with different size and shape are expected to show quantum confinement effect tailoring the optoelectronic properties. But the high temperature synthesis of good quality MAPbBr_3 nanocrystals is challenging, due to the volatile nature of methylamine precursor. In this chapter, we stabilized the precursor at higher temperature by forming methylammonium-oleate salt. By this process, MAPbBr_3 nanocrystals were prepared at higher temperature like 120, 140, and 160 °C. Nanoplatelets with thicknesses 1.9 and 2.3 nm are formed at 120, 140 °C, respectively with excitonic optical absorption and emission similar pseudo 2D layered hybrid perovskites. Whereas, MAPbBr_3 nanocubes are formed at 160 °C. Also, nanoplates are found to form superlattices by stacking, while nanocubes do not. Thus, depending on size and shape of nanocrystals, the optical properties and stacking tendency of MAPbBr_3 vary.

Chapter 5: Thesis Summary and Future Outlook

The summary of all the chapters mentioned above is discussed in this chapter. We have also provided a future outlook of the thesis work.

Appendix A: Photoluminescence of $\text{Cs}_2\text{NaBiCl}_6$ at Cryogenic Temperature

An unusual appearance of photoluminescence from $\text{Cs}_2\text{NaBiCl}_6$ in UV region is observed below 50 K along with a broad emission centered at visible region below 175 K. These unusual emissions are not related to the phase change of $\text{Cs}_2\text{NaBiCl}_6$ around 100 K.

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Chapter 1

Introduction

1.1 Structural Phase Transition

Phase transition is a process of transition between two states with uniform physical properties.¹ The transitions may be between different states of matter (solid, liquid, gas, plasma) or structural (one crystal structure to another), or changes between magnetic ordering (for example, ferromagnetic to paramagnetic).² During a phase transition of a given medium, certain properties of the medium change as a result of the change of external conditions, such as temperature or pressure. In this thesis, we discuss about solid-to-solid phase transition that takes place without involving other states of matter. Usually, crystals acquire one type of atomic arrangement at a particular external condition giving rise to a crystal structure. For example, common salt, sodium chloride (NaCl) acquires face centered cubic crystal structure at room temperature in solid phase with six Cl^- ions surrounding one Na^+ ion and vice versa. Upon changing the external condition like temperature, pressure it acquires another crystal structure by either rearrangement or by changing their position by rotation or translation in space. There are several possibilities of changing the space group among them. Any such transition can be termed as “phase transition.” There are 7 crystal systems (cubic, hexagonal, tetragonal, trigonal, orthorhombic, monoclinic, and triclinic) available as shown in Figure 1.1.

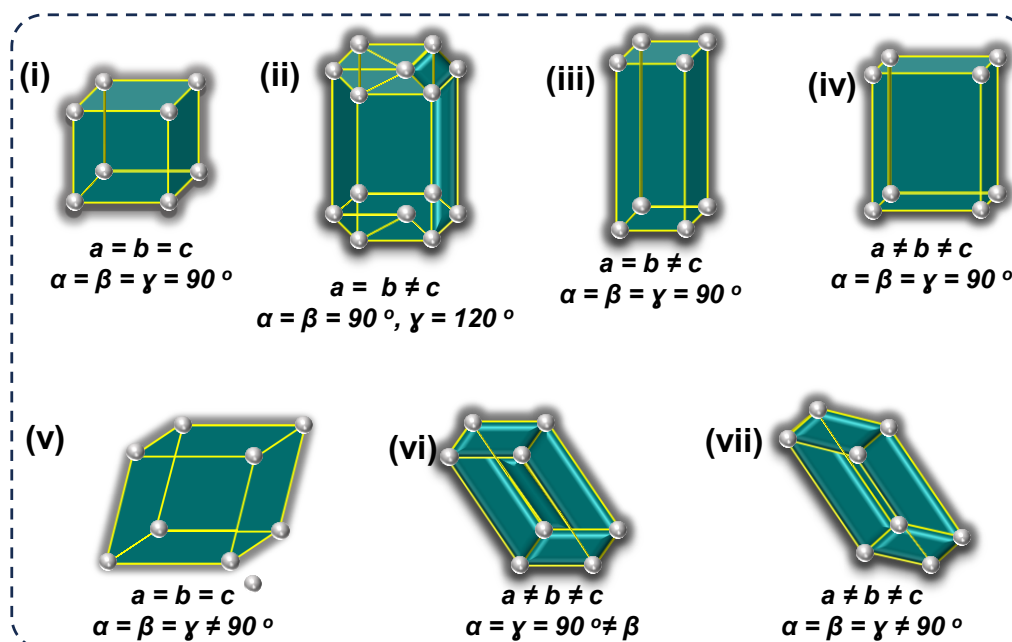


Figure 1.1: The 7 crystal systems: (i) cubic, (ii) hexagonal, (iii) tetragonal, (iv) orthorhombic, (v) rhombohedral, (vi) monoclinic, (vii) triclinic. Gray spheres are atom/ion and green is the unit cell.

Chapter 1

Introduction

Why the phase transformations are important to understand while it is not a very unique property of materials? There are plenty of examples, where the system undergoes phase transition from one crystal system to another. For example, the first scientific report on solid to solid phase transition was observed in Sulphur, discovered by Eilhard Mitscherlich in 1823 from orthorhombic to monoclinic system at 95.6 °C.³ This was followed by crystal structure change in tin paste from metallic white tin (β -tin) which is tetragonal to semiconducting gray tin (α -tin, cubic) below 13.2 °C.⁴ Thus, these phase transitions are important in terms of applications, based on their physical properties.

Now, to define a phase transition, a “phase” should be defined. The arrangement of atoms by repetition of which a crystal grows, is called a unit cell. The crystal systems (in Figure 1.1) differ by the lattice parameter (edge length of unit cell) a , b , c in three dimensions and the angle between the axes, α , β and γ . The gray circles at the corners indicate atoms or ion present in unit cell. For the seven crystal systems, there are fourteen Bravais lattices in three-dimension (3D). For cubic systems, (i) simple cubic, (ii) body-centered cubic, (iii) face-centered cubic, for tetragonal system, (i) simple tetragonal and (ii) face-centered tetragonal, for orthorhombic, (i) simple, (ii) Base-centered, (iii) body-centered and face centered orthorhombic lattices are there. Likewise for all other four crystal systems depending on atomic arrangement give rise to 14 Bravais lattice. For simplicity the three Bravais lattice of cubic crystal system is shown in Figure 1.2. Each of the seven crystal systems or fourteen Bravais lattices represent a single phase of a material at a particular external condition.

Changes from one sub-lattice to another arrangement of atoms is also termed as phase transition. For example, Zircon (ZrSiO_4) transforms from a tetragonal primitive (simple tetragonal, Figure 1.2.iv) lattice (zircon structure) to a tetragonal body-centered (Figure 1.2.v) lattice (scheelite structure, like CaWO_4) under high pressure.⁵ Likewise without changing the atomic arrangement the same crystal system or lattice may undergo a change in lattice parameter or symmetry operation change which give rise to 230 space groups out of these 7 crystal systems in three dimensions. For example, cubic, tetragonal, orthorhombic crystal system consists of 36, 68 and 59 space groups, respectively.⁶ Any transformation between 230 space group under the

external stimuli is considered as phase transition, this may give rise to difference in physical and chemical properties.

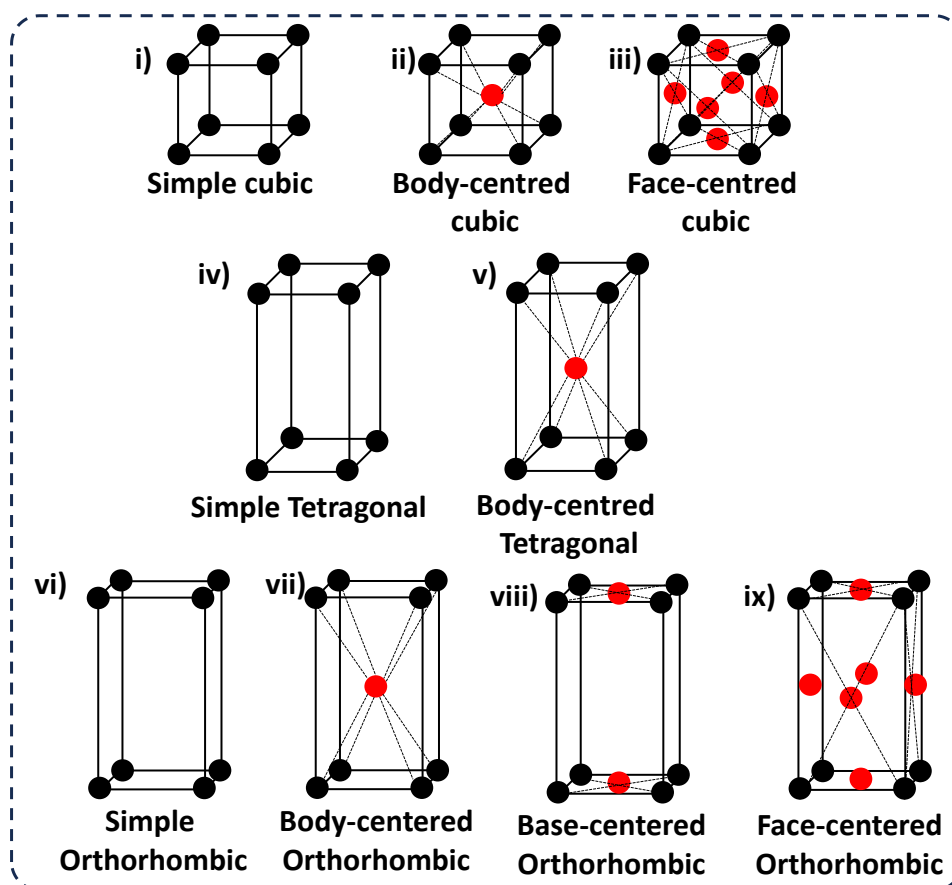


Figure 1.2: Bravais lattice of (i-iii) cubic, (iv,v) tetragonal, (vi-ix) orthorhombic crystal systems.

While this structural transition is very common for crystals under external condition variation, some systems need very harsh condition to undergo crystal structure change. For example, Body-centered cubic ferromagnetic α -iron converts to face centered paramagnetic γ -iron and body-centered paramagnetic δ -iron at 910 °C and 1394 °C respectively.⁷ Other than magnetic and dielectric property, photophysical property of materials is expected to change with phase transformation. For that we need such systems which show phase transition easily at ambient or mild conditions like at room temperature or lower temperature such that the in photophysical property retains without quenching and fine structured changes in such properties due to phase transition can be tracked. Perovskites are such systems which usually undergoes phase transition even at room temperature or below, so that structure-photophysical property relationship study become doable.

1.2 Perovskites

Perovskite is a calcium titanium oxide mineral composed of CaTiO_3 discovered in Ural mountain in Russia by Gustav Rose in 1839 and named after Russian mineralogist Lev Perovski.⁸ The ideal perovskite-type structure is cubic with a space group $Pm\bar{3}m-O_h$. It has general formula of ABO_3 where B has +4 oxidation state and 6 coordination, forming octahedra with 6 O^{2-} . A site cation has +2 oxidation state and 12 coordination, sitting at the center of cube formed by 8 BO_6^{6-} octahedra (illustrated in Figure 1.3).⁹ Perovskite structure can be formed out of oxide and halide compositions. For halides, the formula evaluates as ABX_3 , where A is monovalent cation, B is bivalent cation, X is monovalent anion.

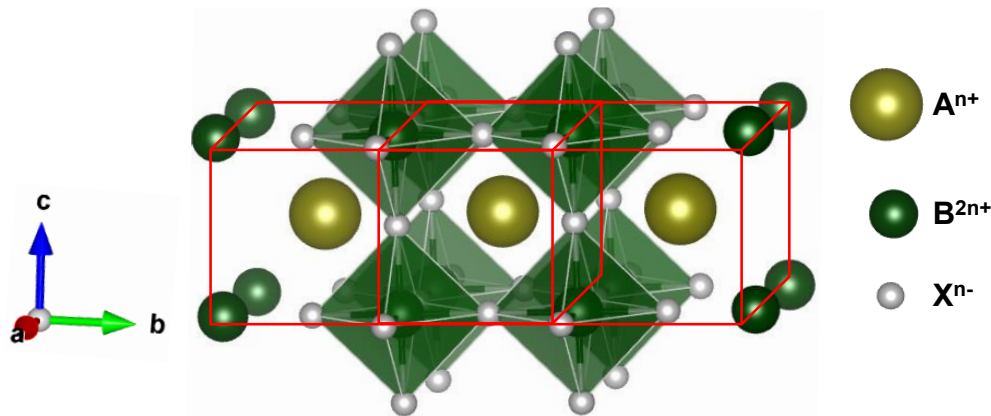


Figure 1.3: Ideal perovskite structure showing three dimensionally connected BX_6^{n-} octahedron, A site cation in between 8 octahedra.

But each element present in periodic table who satisfies the oxidation states required to form ABX_3 , cannot form perovskite structure. The other important parameter that determines whether the three-dimensional perovskite structure will form or not is the radius of A site, B site cation, and X anion. Goldschmidt's tolerance factor indicates the stability and the distortion of the crystal especially of ABX_3 type crystal structure, that was first described by, Victor Moritz Goldschmidt in 1926,¹⁰ and expressed as,

$$\tau = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (1)$$

where r_A and r_B represent ionic radius of larger or A site cation, smaller or B site cation respectively, r_X ionic radius of X site anion. For ideal cubic perovskite structure the Goldschmidt tolerance factor should come between 0.8 to 1.¹¹

Oxide perovskites have been extensively studied like SrTiO_3 as superconductor,¹² in ferroelectrics and capacitor, transducers¹³ and various other applications like in fuel cell and battery electrode materials,¹⁴ heterogeneous catalysis¹⁵ since the last century. Halide perovskites are known since late 18th century but were not explored significantly till 19th century. Since early 20th century, due to interesting electrical and optical property halide perovskites started to gain attention and the exploration has grown exponentially. Halide perovskites' optoelectronic property hugely depends on the crystal structure, yet to be explored.

1.3 Electronic Band Structure of Halide perovskites

Halide perovskites have their chemical formular as ABX_3 where A is monovalent cation like Cs^+ , Rb^+ , MA^+ (MA: methylammonium, CH_3NH_3^+), FA^+ (FA: formamidinium, $\text{NH}_2\text{CHNH}_2^+$), B is bivalent cation like Pb^{2+} , Sn^{2+} , Ge^{2+} and X is Cl^- , Br^- or I^- .^{16, 17} B site cation with six halides forms the octahedra connected three dimensionally, with the A site cation sitting in between the octahedra as shown in Figure 1.3.

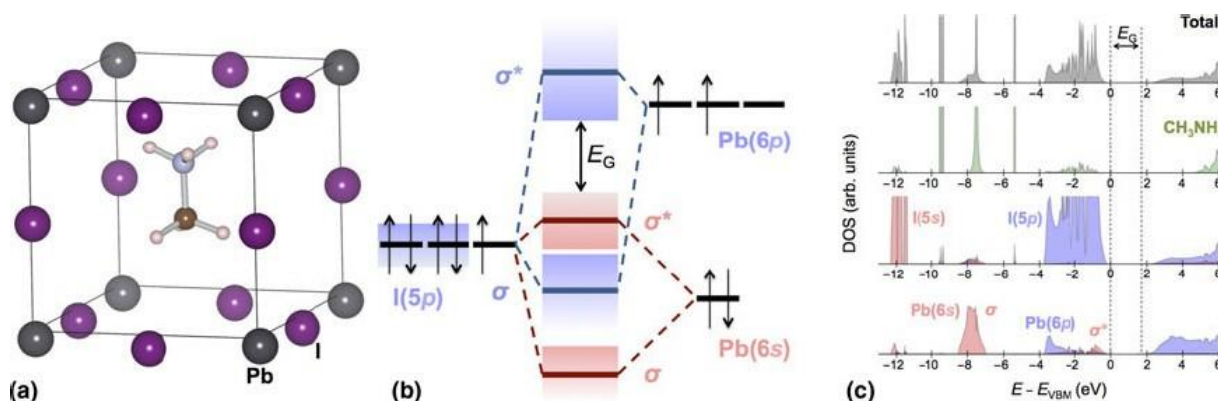


Figure 1.4: (a) Crystal structure of MAPbI_3 where the MA^+ sits in the center of cube (yellow circles are H atom, light blue is N). (b) Energy bands formed by molecular orbitals of 6s and 6p orbital from Pb and 6p from I. (c) Computed density of states MAPbI_3 separated into A site cation and s and p orbitals including spin-orbit coupling. The MA^+ cation does not introduce states at the band edge. Reprinted with permission from reference.¹⁸ Copyright © 2015, The Materials Research Society.

When A site cations are Cs^+ and Rb^+ , the perovskites are all inorganic one while MA^+ and FA^+ forming lead or tin halide framework is called “organic-inorganic hybrid.” With such variety of A site cations, why essentially lead, tin and germanium have been chosen as the metal center for halide perovskite as B site cation? The above mentioned three elements are from Group 14 with ns^2np^0 configuration in +2 state. When they form bond with halides forming octahedra, as shown in Figure 1.4a, the s

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and p orbitals ($6p$ and $6s$ of Pb, $5p$ and $5s$ of Sn) overlaps with the surrounding halide ions' p orbitals ($3p$ of Cl, $4p$ of Br, $5p$ of I).¹⁸ Let us take an example, formed from the above combinations of A, B and X, MAPbI_3 , where $6s$ and $6p$ of Pb and $5p$ of I form bonding (σ) and antibonding (σ^*) molecular orbital out of one octahedra (brown and blue horizontal lines in Figure 1.4b). When the Pb-I octahedra are repeated and three dimensionally connected, the molecular orbitals come closer and transform to bands. The highest occupied band formed by antibonding molecular orbitals (σ^* brown in Figure 1.4b) are valence band, and the lowest unoccupied band formed by antibonding from ($5p$ and Pb_{6p}) forms conduction band (σ^* blue in Figure 1.4b). The difference between valence band and conduction band is the bandgap (denoted by E_g). Figure 1.4c shows the contribution of s and p orbitals from Pb and halide and MA (CH_3NH_3^+), where the minima of conduction band and maxima of valence band mostly comprise of Pb and halide.

In addition, the large polarizability of ns^2 ions like Pb, Sn, Ge in +2 oxidation states leads to spin orbit coupling increasing the bandwidth of conduction band while filled ns orbital leads to dispersive valence band due to heavier effective mass (Figure 1.7d).¹⁸ Increment in the bandwidth of conduction band leads to increment in carrier mobility. So, heavier elements like Pb, Sn, Ge are essentially chosen for semiconducting applications. Also, the perovskites formed from Pb, Sn, Ge are direct bandgap semiconductors, meaning the conduction band minima (CBM) and valence band maxima (VBM) having the same k point (Figure 1.5) The carriers, that is electrons and holes are created upon excitation of the materials with the energy equal or greater than its bandgap (E_g in Figure 1.5) which are shown with different color coded arrows indicating higher energy of excitation. The emission process happens from the minima to maxima of conduction and valence band respectively and from nowhere else. Essentially, the band edges (CBM and VBM) have low no or contribution from A site cation. As the halide changes, the overlap changes between metal and halide orbitals, giving rise to different values of E_g .¹⁸ Still variation in A site cation's size or radii alters the space among the lead halide octahedra, thereby altering octahedra tilting, so the crystal structure may change which may lead to the change in absorption or emission processes.

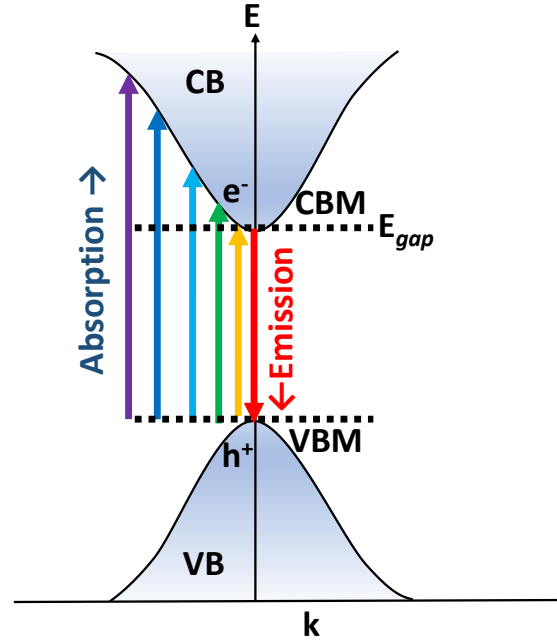


Figure 1.5: (a) Absorption (Violet, navy blue, sky, green, yellow arrows in order of decreasing energy) and emission (red arrow) in E-k diagram of a direct bandgap semiconductor. K represent the wave vector of the lattice.

For example, at room temperature, CsPbBr₃ crystalizes in orthorhombic crystal structure¹⁹⁻²⁵ while changing A site cation from Cs⁺ to MA⁺ changes the crystal structure to cubic.²⁶⁻²⁸ Even these two different crystal structures may lead to tune electronic band structure giving different optical properties arising from their band edges like CBM and VBM. Meaning, excitation of the charge carrier (absorption) or recombination of them (emission) as shown in Figure 1.5, may change due to structural change.

1.4 Size and Shape Effect on Optoelectronic Properties

Absorption of photon energy equal or greater than the bandgap (E_g) of a semiconductor, excites electron from VBM to CBM leaving positively charged holes in VBM forming an exciton (an electron-hole pair bound by Coulomb interaction). The carriers, electron and hole move freely three dimensionally in bigger sized perovskite semiconductors (bulk). As the size of semiconductor decreases the electron and hole are confined and bound more strongly by Coulombic interaction (forming exciton),²⁹ more is the required energy to separate the electron and hole, higher is the band gap. The bandgap of semiconductor is related size following Brus equation,³⁰

$$\Delta E = E_g + \frac{\hbar^2}{8r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \quad (2)$$

Where ΔE and r are the bandgap the radius of semiconductor nanocrystals (NCs), E_g and the bandgap of bulk semiconductor, $\hbar$ is Planck's constant, m_e^* and m_h^* are effective mass of electron and holes, specific to the material. As shown in Figure 1.6a, with decreasing radius of NCs starting from bulk, the confinement bandgap and exciton binding energy increases, along with increase in the discreteness of energy levels near bandgap.²⁹ The size below which the NCs show quantum confinement, is called "Bohr radius". Exciton behaves like hydrogen atom (one positively charged nucleus like hole and negatively charged electron) when confined in a NCs less than Bohr radius of that semiconducting material (comparable to a hydrogen atom).²⁹ In bulk charge carriers move freely in band-continuum (bulk semiconductor in Figure 1.6a left), decreasing size introduced molecular like states near bandgap with increasing bandgap (towards molecule in Figure 1.6a middle panel).

Alongside the size effect, the shape also introduces the quantum confinement effect. In 3D bulk charge carriers move freely in three dimensions with lowest Coulombic attraction and binding energy as they are confined in no directions and thereby density of states (DOS) increases at higher energy continuously (Figure 1.6b, bulk semiconductor). In two-dimensional (2D) platelet where the lead-halide octahedral network thickness is lesser than Bohr radius of the material the charge carriers or exciton are confined in two dimensions, so they can move only in two dimensions and confined by one dimension. So the Coulombic interaction or the energy required to make the carriers free is higher as compared to 3D bulk. The DOS and energy become discontinuous along the third direction and looks like steplike increment (Figure 1.6b, quantum well).³¹ For one-dimensional (1D) quantum well (Figure 1.6b) the charge carriers or exciton are confined in one-dimensional metal-halide octahedral network and move freely in one dimension only. They are confined from other two directions. As a result, the energy versus DOS are discontinuous in other two directions. For zero-dimensional (0D) the excitons are confined from all three directions with strongest Coulombic interaction between electron and hole, and energy levels appears like discrete, as in molecules.

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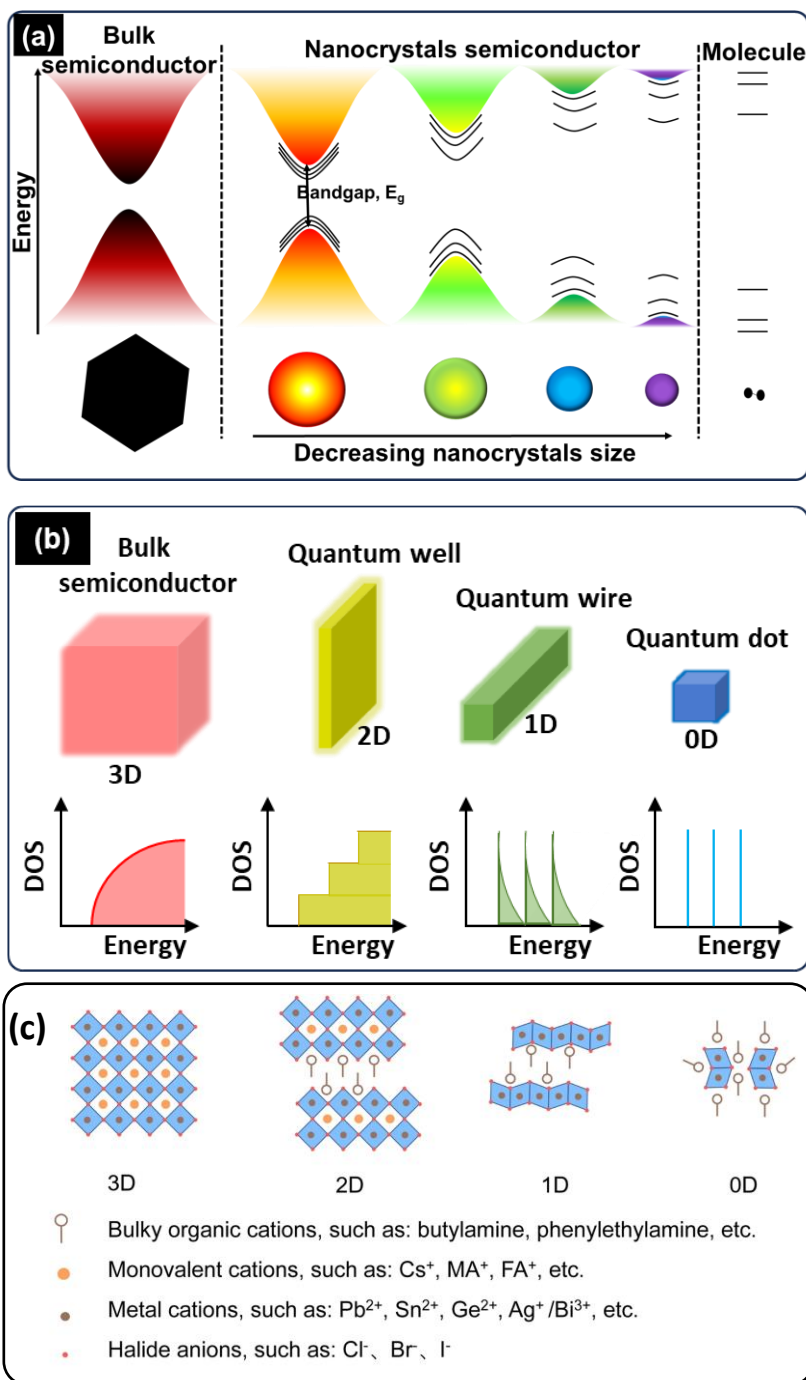


Figure 1.6: (a) Schematic representation of quantum confinement effect: the bandgap of semiconductor NCs increases with decrease in size also discrete energy levels arises near bandgap. (b) Different shapes of semiconductor from 3D bulk to 2D nanoplatelets to 1D quantum wire to 0D quantum dot with increasing quantum confinement. (c) Quantum and dielectric confinement in low-dimensional halide perovskites with organic spacer cations. Reprinted with permission from reference.³² Copyright © 2023, The Author(s).

These different shaped perovskites are very much dependent on the synthesis procedure. The size and shape of perovskite from bulk to nano can be controlled by maintaining the temperature, ligands (capping ligands surrounds NCs as well as A site

cation). Figure 1.6b explains the reduction in dimensionality by changing the shape and size from bulk to 2D nanoplatelets to 1D quantum wire to 0D quantum dot with increasing quantum confinement, keeping the compositions same, for example, all for CsPbI₃. Also changing A site cation to larger ones exceeds the Goldschmidt tolerance factor destroying the 3D connectivity by scissoring the 3D perovskite into 2D connected octahedra separated by long chain organic cations. As shown in Figure 1.7c, further increase in A site cation size or stoichiometry reduce the dimensionality from 2D to 1D and even 0D introducing strong quantum confinement in low-dimensional bulk systems.

1.5 Structural Effect on Optoelectronic Properties

To understand structure-property relationship and its impact on device applications, let us take an example of bulk CsPbI₃. Because among the huge number of halide perovskites of different combinations of A, B and X, iodide base perovskites are ideal because of highest carrier mobility. Among possible iodide-based perovskites (CsPbI₃, CsSnI₃, CsGeI₃), Sn, Ge based perovskites suffer from oxidation instability, i.e. Sn²⁺/Ge²⁺ converts to Sn⁴⁺/Ge⁴⁺ and loses the three-dimensional perovskite structure. Thereby CsPbI₃ is one of the most promising candidates for solar cell due to its lowest bandgap, high carrier mobility due to good Pb-I overlap.

Figure 1.7a shows the schematic representation of different phases of CsPbI₃ perovskite. Among the four phases, α -cubic, β -tetragonal, γ -orthorhombic are formed by corner shared lead-iodide octahedra and are semiconducting in nature. The δ -phase formed by edge shared lead-halide octahedra in one dimension is not a semiconductor at all and cannot be used in device like solar cell. Among the three semiconducting phases α (cubic) phase has the best overlap between orbitals of Pb and I with a Pb-I-Pb bond angle 180°, as shown in Figure 1.7b. As the symmetry decreases from cubic (above 360°C) to tetragonal (above 275°C) to orthorhombic at lower temperatures (above 120°C)³³ (see Figure 1.7c) the overlap decreases with lowering the bond angle (Θ in Figure 1.7b) thereby enhancing the bandgap.³⁴ The cubic phase having the most effective overlap between lead halide orbitals, has the lowest bandgap, 1.26 electron-volt (eV), making it ideal for solar cell application, while the bandgap increases towards orthorhombic phase. So, it is important to stabilize α -CsPbI₃ at room temperature.

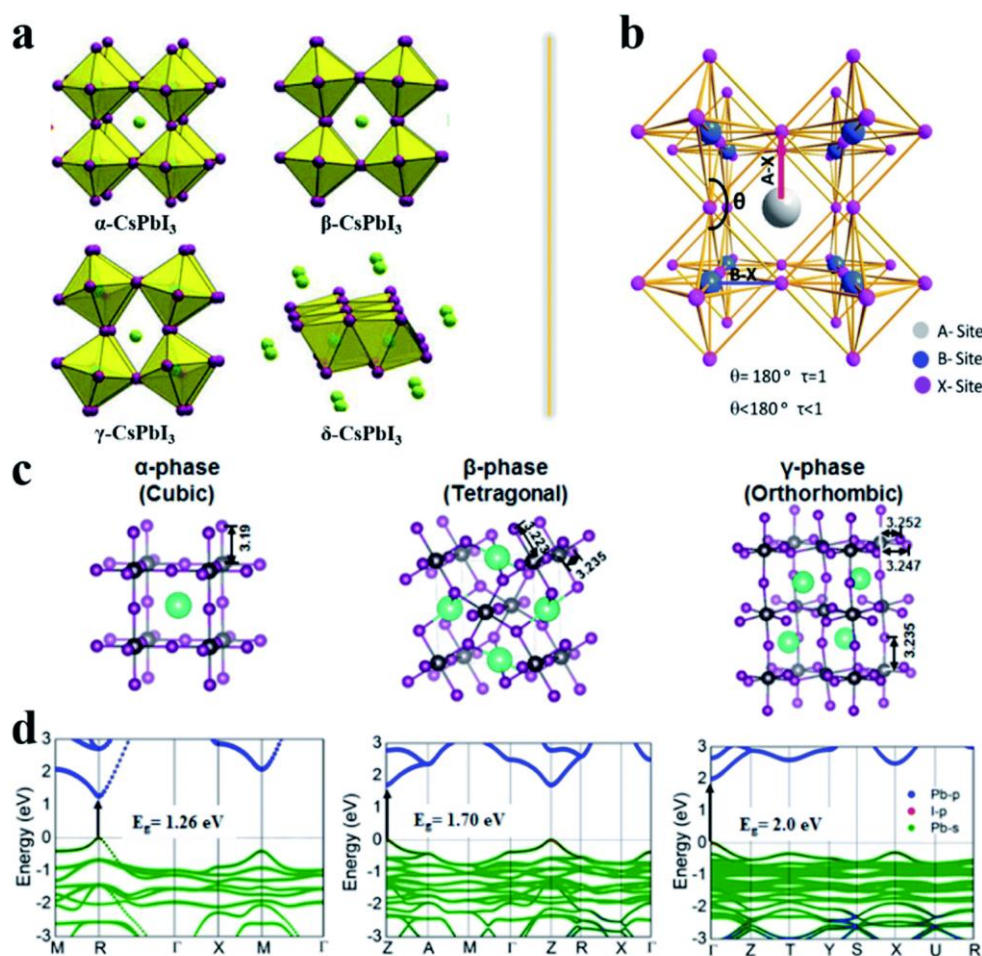


Figure 1.7: (a) Schematic representation of three semiconducting phases, cubic (α), tetragonal (β), orthorhombic (γ) and one non-semiconducting orthorhombic (δ) phase, (b) Bond length and bond angle in perfect cubic perovskite, (c) Bond angles and Pb-I overlap in cubic, tetragonal, and orthorhombic phases. (d) Evolution of bandgaps with lowering the symmetry from cubic to tetragonal to orthorhombic phase. Reprinted with permission from reference.³³ Copyright © 2021, Royal Society of Chemistry.

1.5.1 Doping Effect on Structural Phase Transition

The α -phase of bulk CsPbI₃ is unstable and converts to non-semiconducting δ -phase at room temperature and difficult to fabricate device out of it. The main reason of the instability is the deviation of Goldschmidt tolerance factor (τ) from the range of 0.8-1. The factor is expressed as shown in equation (1)

$$\text{Goldschmidt tolerance factor, } \tau = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad \text{eq (1)}$$

where r_A and r_B represent ionic radius of larger or A site cation, smaller or B site cation respectively, r_X is ionic radius of X^- . Due to smaller size of Cs^+ ion than Pb-I octahedra, to cover extra space around Cs^+ , the octahedra tilts towards each other causing phase

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instability (Figure 1.8b). As the B-X-B angle (θ) decreases, τ decreases (Figure 1.8a). To overcome this problem radius of A site can be increased by replacing with larger organic cation, then it causes the thermal instability issue.³⁵ Rather, B-X octahedra can be squeezed to restrict tilting around Cs^+ ions (Figure 1.8b). Replacing Pb^{2+} (Shannon radii 119 pm) partially with smaller sized Mn^{2+} (83 pm), increases the tolerance factor, stabilizing the α phase.³⁶ As a result, although bare CsPbI_3 loses its luminescence property within 10 days, as shown in Figure 1.8c, whereas upon 4.8% Mn^{2+} doping the photoluminescence property almost retains unchanged up to 17 days.³⁷ The photoluminescence stability indicates the α -phase stability of CsPbI_3 , since conversion to δ phase makes CsPbI_3 non photoemissive in nature.

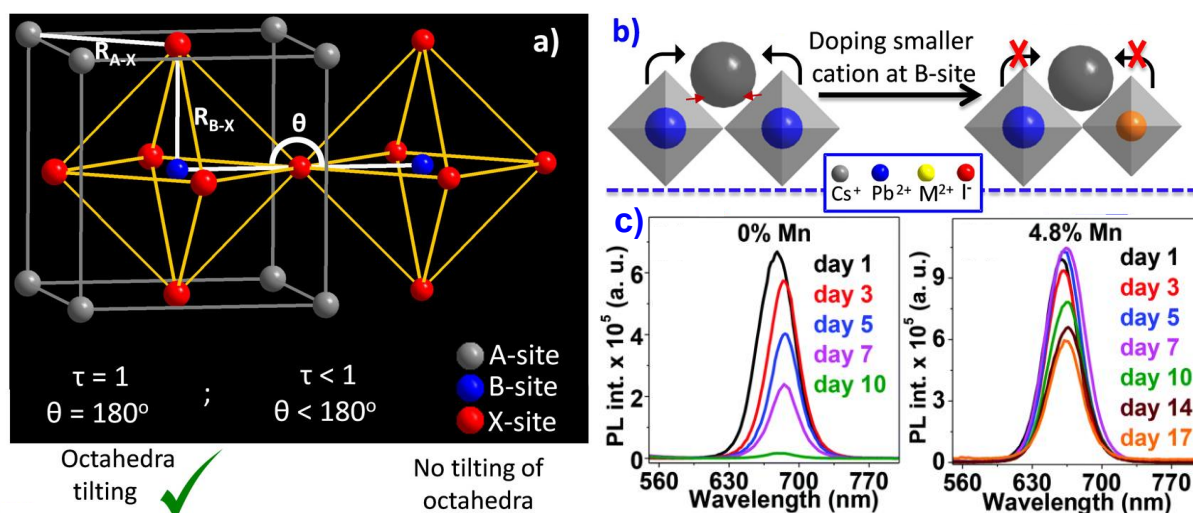


Figure 1.8: Pictorial representation of (a) relation of tolerance factor (τ) with B-X-B bond angle (θ) of the ABX_3 perovskite structure (b) $[\text{BX}_6]^{4-}$, $(\text{PbX}_6)^{4-}$ octahedral tilting restricted by substituting B site cation with smaller sized Mn^{2+} cation which reduced the octahedral volume. Reprinted from reference³⁶ with permission. Copyright © 2018, American Chemical Society (c) Comparison of photoluminescence stability of Undoped and 4.8% Mn^{2+} doped CsPbI_3 under ambient condition. Reprinted from reference³⁷ with permission. Copyright © 2019, Royal Society of Chemistry.

1.5.2 Size Effect on Structural Phase Transition in Perovskite

Not only doping or alloying with foreign elements like the example given above for Mn-doped CsPbI_3 , decreasing the size from bulk towards nanometre scale also reduces the phase transition tendency of the material as observed experimentally.^{38, 39} Other than the difference in optoelectronic properties like quantum confinement, the surface termination and surface to volume ratio make a significant difference in structural aspect between bulk and NCs. Both the bulk and NCs terminate at their

surfaces with uncoordinated bonds (as shown in Figure 1.9). For example, I^- (violet spherical atoms in Figure 1.9) at core has 2 coordination shared with two Pb^{2+} ions (light green spherical atoms) in both sides while at surface I^- is bound to only one Pb^{2+} . So, coordination of I^- at surface is unsatisfied, possessing one dangling bond. In some cases passivating ligands in NCs with the help of non-covalent interactions passivate those dangling bonds on NCs surface.⁴⁰ Uncoordinated or dangling bonds create defect sites on the surface when compared with the fully coordinated core atoms of bulk or NCs. The fraction of uncoordinated atoms or defects on surface versus fully coordinated atoms in core is higher in NCs than bulk, because the surface to core or surface to volume ratio increases in many folds in NCs than bulk. This is the key factor which regulate the thermodynamic or kinetic feasibility of stabilizing one state or in other words conversion of one phase to another.⁴¹⁻⁴³

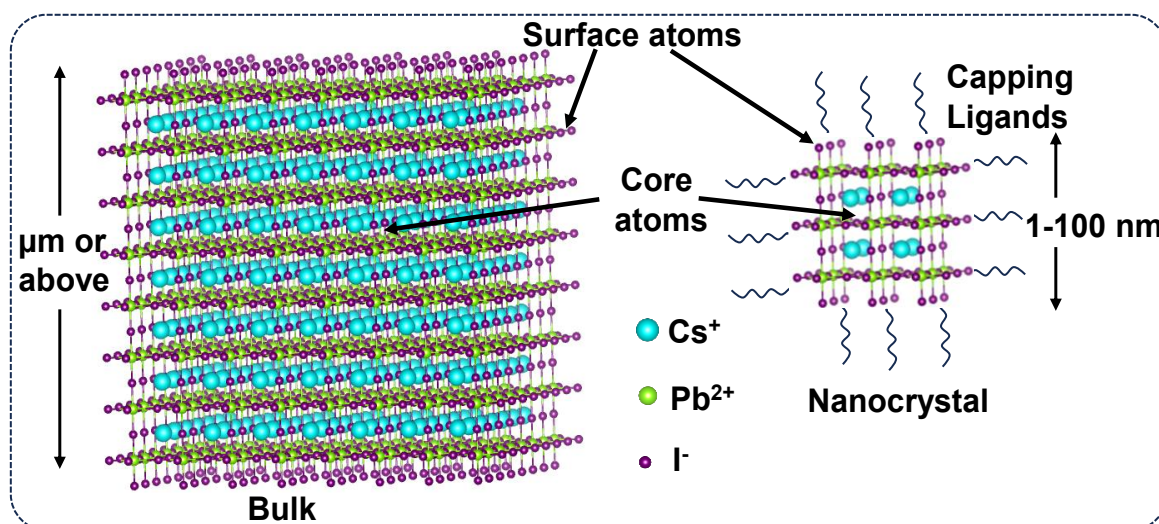


Figure 1.9: Structural difference between cubic CsPbI_3 bulk and NCs (reference taken from mp-1069538), left side schematic represents bulk CsPbI_3 in ball and stick model with dangling bonds at surface while fully coordinated bonds in core, right side schematic represents NCs with capping ligands passivating dangling bond with much higher surface to core atom ratio than bulk.

1.6 Double Perovskites

Due to oxidation instability of +2 state Sn/Ge are often less preferred as compared to Pb based halide perovskite.⁴⁴ But lead has serious concern with its toxicity. Essentially lead can mimic some biologically essential cation like Ca^{2+} , Fe^{2+} , Zn^{2+} disrupting the physiological functions such as neurological disorders, high blood pressure, kidney damage, and anemia.^{45, 46} Thereby as an alternative of perovskite a new kind of perovskite was found where two consecutive bivalent metal ions are

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replaced with one monovalent and trivalent metal ions. For example, two consecutive Pb^{2+} ions can be replaced with one B^+ ion and one B^{3+} ions and the ABX_3 formula is doubled to $\text{A}_2\text{B}^+\text{B}^{3+}\text{X}_6$ as shown in Figure 1.10. These double perovskites are environmentally benign.⁴⁷

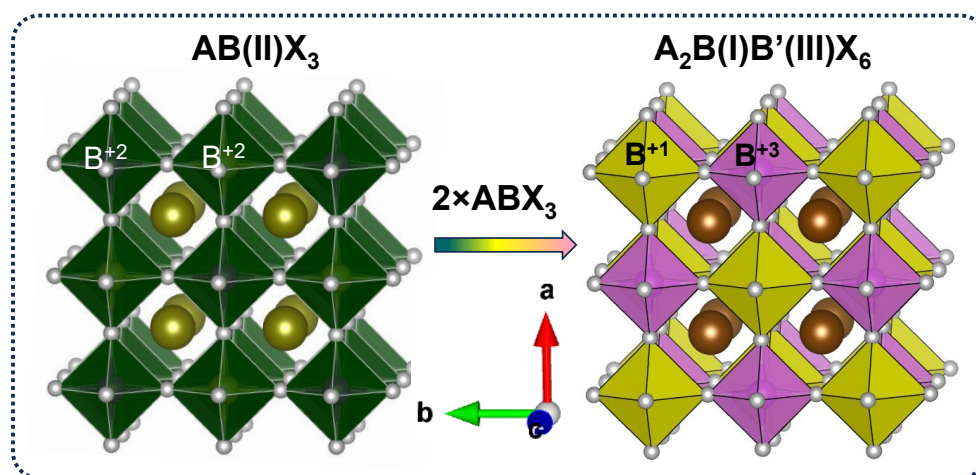


Figure 1.10: Evaluation of double perovskites ($\text{A}_2\text{B}^{+1}\text{B}^{+3}\text{X}_6$) from perovskites (ABX_3). In perovskites green coloured octahedra are $[\text{BX}_6]^{4-}$, in double perovskites alternative yellow and orchid coloured octahedra are $[\text{BX}_6]^{5-}$ and $[\text{BX}_6]^{3-}$ respectively.

There are several elements possessing stable +1 and +3 required for forming consecutive $[\text{BX}_6]^{5-}$ and $[\text{BX}_6]^{3-}$ octahedra in double perovskites. But all elements in periodic table having +1 or +3 oxidation state, cannot form double perovskite. Theoretically, hundreds of compositions have been predicted based on their thermodynamic stability.⁴⁸ Many of the predicted composition have been reported experimentally, still many are unexplored. Similar composition of K_2NaAlF_6 was first found in Colorado back in 1883 and referred to as Elpasolite.⁴⁹ Although among the possible compositions, some double perovskites have indirect band gaps, limiting their applications. Based on their structural stability and applications, some are explored and listed in the Figure 1.11 with following color codes combination following the chemical formula. Possessing two kinds of metal centers, double perovskites or elpasolite allow wide range of compositions along with variety of choices for dopants to incorporate new property in the host. In Figure 1.11, the light blue colored elements have been used to form at least one composition of elpasolite experimentally. The coloured triangle at the corners of each elements indicates their position in double perovskite as coded in the above formula $\text{A}_2\text{B}^+\text{B}^{3+}\text{X}_6$.

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1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															

NH₄⁺

CH₃NH₃⁺

Figure 1.11: The possible elements forming double perovskite in periodic table with the chemical formula $A_2BB^{3+}X_6$. The light blue coloured elements have been reported to form at least one double perovskite composition experimentally. The coloured triangles indicate the position of the element in double perovskite (Blue triangle as A site cation, red triangle as monovalent B site cation, the green triangle as trivalent B^{3+} and orange triangle as X site anion). Reprinted from reference⁵⁰ with permission. Copyright © American Chemical Society.

In double perovskite the $[BX_6]^{5-}$ and $[BX_6]^{3-}$ octahedra formed by monovalent and trivalent metal ions are arranged in alternative way in three-dimensional $2 \times 2 \times 2$ supercell as shown in Figure 1.12. For example, $Cs_2AgBiCl_6$ shows six possibilities to arrange these two types of metal centers, ($AgCl_6^{5-}$ and $BiCl_6^{3-}$) as shown in Figure 1.12 (A-F). Among all these six arrangements, energetically most preferable arrangement is where the monovalent and trivalent metal ions form alternative octahedra, Figure 1.12(F), as theoretically predicted. Experimentally, for example by solving the single crystal experiment for plenty of double perovskite, the alternative arrangement of octahedra with +1 and +3 metal ions have been observed. Though the difference in energy between other arrangement (A-E in Figure 1.12) is very less, around tens of meV, those may also be plausible form of double perovskite structure though experimentally not observed yet.

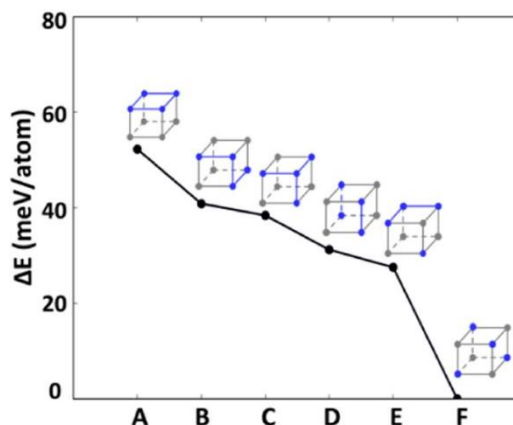


Figure 1.12: Each cube shows the possible arrangement of AgCl_6^{5-} (gray dot) and BiCl_6^{3-} (blue dot) in double perovskites. The difference in corresponding total energy of the arrangements (A, B, C, D, E and F) are calculated ΔE (meV/atom). Reprinted from reference⁵¹ with permission. Copyright © 2017, American Chemical Society.

Likewise, the conventional perovskites, the structural stability of a double perovskite is also determined by Goldschmidt tolerance factor and octahedral factor.⁵² From single metal center forming octahedra in perovskites, the formula is extended for two types of metal centers forming octahedra in double perovskite as,

$$\text{Goldschmidt tolerance factor, } \tau_{dp} = \frac{r_A + r_X}{\sqrt{2}(\frac{r_B + r_{B'}}{2} + r_X)} \quad (3)$$

$$\text{Octahedral factor, } \mu = \frac{r_B + r_{B'}}{2r_X} \quad (4)$$

where, τ_{dp} is the Goldschmidt tolerance factor for double perovskite, r_A , r_B , $r_{B'}$ and r_X are the ionic radii A^+ , B^+ , B^{3+} and X^- . From the existing set of perovskite and double perovskites, it is found that the structure is stable if the condition for octahedral factor $0.44 < \mu < 0.90$ and Goldschmidt tolerance factor $0.81 < \tau < 1.11$ is satisfied.⁵¹

1.7 Structural Phase Transition in Double Perovskites

Like perovskites, double perovskites also undergo change in crystal structure upon variation of external conditions like temperature and pressure. Usually at room temperature double perovskites tend to crystallize in cubic structure⁵³⁻⁵⁷ while some of the double perovskites adopt tetragonal crystal structure when temperature is lowered.^{58, 59} As an example, let us take $\text{Cs}_2\text{NaBiCl}_6$ crystal structure as shown in Figure 1.13. The two metal centers, Na and Bi, red, and yellow spherical atoms, form six coordinated corner-shared octahedra with six halides (Cl here, green spheres) and

extend in three dimensions forming double perovskite. The polyhedral (octahedra here) have been removed to make the changes in the atomic coordinates or bonds visible upon phase change from cubic to tetragonal, and presented in ball and stick model. It is found that the structural change in $\text{Cs}_2\text{NaBiCl}_6$ double perovskite happens by rotation of octahedra in unit cell and elongation of unit cell along one axis out of three as depicted in Figure 1.13. Along ab plane the unit cell is rotated thereby changing the atomic coordinates (Cs^+ , Na^+ , Bi^{3+} , Cl^-) (above panel) and perpendicular to ab plane, along c -axis the elongation (bottom panel) following a screw like symmetry operation to change the structure from cubic ($Pm-3m$) to tetragonal ($I4/mmm$).

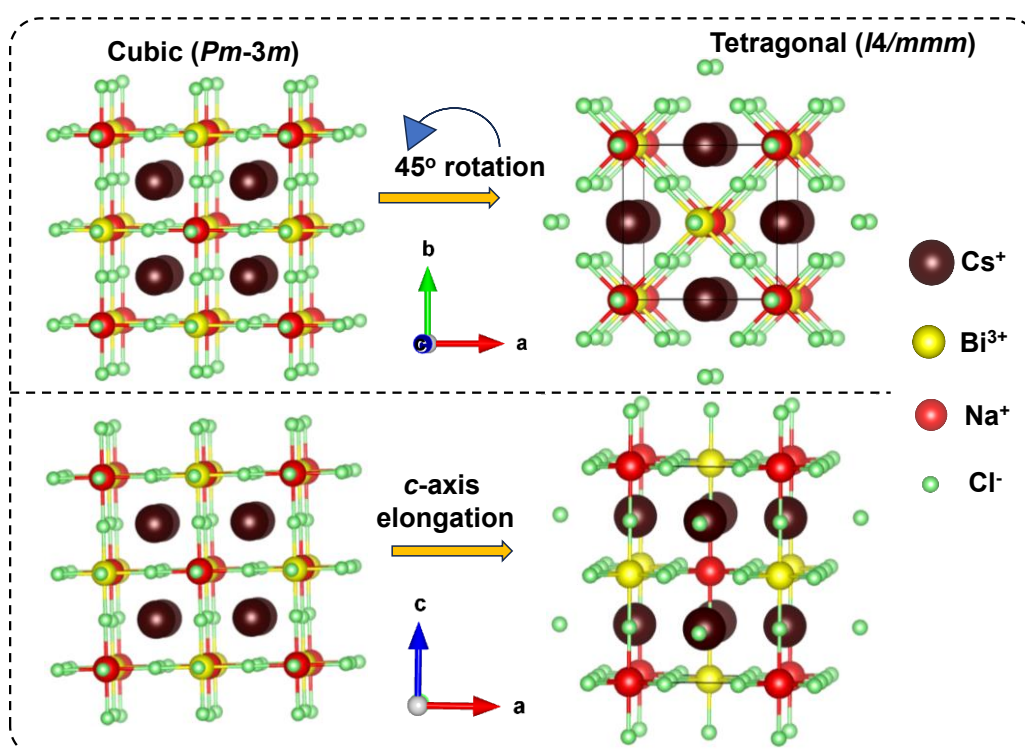


Figure 1.13: The stepwise structural change from cubic ($Pm-3m$) to ($I4/mmm$) for $\text{Cs}_2\text{NaBiCl}_6$ from Crystallographic information file (CIF) recorded at 300 K and 15 K respectively. Unit cell rotation by 45° (above panel) and elongation perpendicular to rotation plane (bottom panel).

1.8 Crystal Structure vs. Electronic Band Structure of Double Perovskites

The structural phase transition affects directly the electronic band structure of perovskite, tuning their optoelectronic properties as discussed above in section 1.5, for example in CsPbI_3 or other perovskites like MAPbBr_3 .⁶⁰ This change especially in optical properties are probed by temperature or pressure dependent abruptness in bandgap (absorption) and or photoluminescence measured. But due to involvement

of two different metal ions with different valence orbitals in double perovskites the electronic band structures differ from single metal ions-based lead halide perovskites. Their optoelectronic properties and their dependence on structure are much different than lead base halide perovskites, discussed earlier. Different energy valence orbitals coming from B site monovalent (Ag^+ , Na^+) and B' site trivalent (In^{3+} , Sb^{3+} , Bi^{3+} etc.) contribute to CBM and VBM. The band structure of some of the compositions are shown in Figure 1.14. Also depending on halide, from Cl to Br to I to metal halide overlap changes modifying the electronic band structure modulating optoelectronic properties.

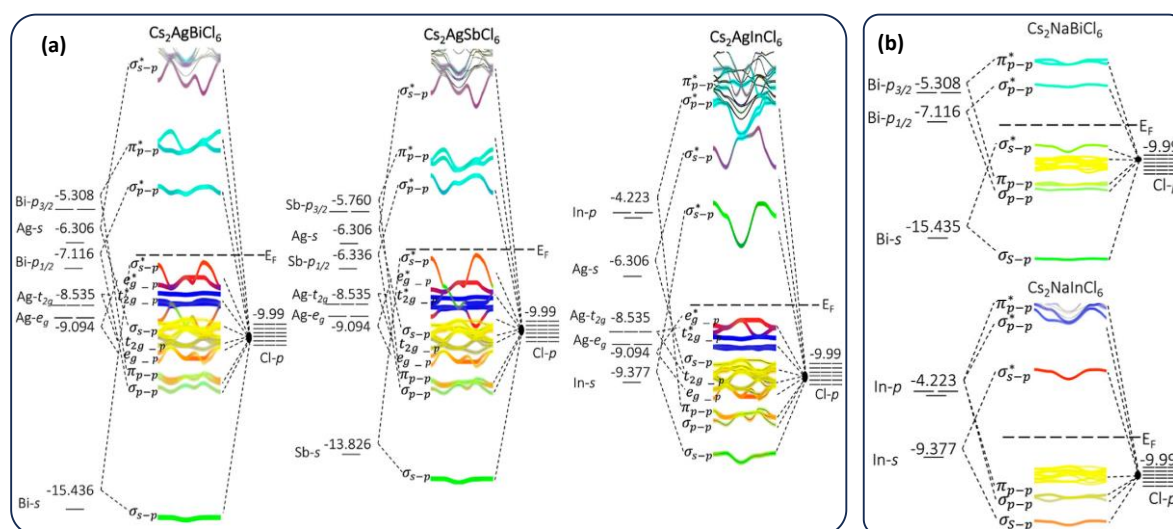


Figure 1.14: (a) Band projected molecular orbital picture of Ag based halide double perovskites formed by molecular hybridization of B site cation (Ag)- {s, d}- Cl(p), B' site cation (Bi, Sb, In)- {s, p}-Cl-p atomic orbitals forming bonding and antibonding orbitals. (b) Band projected molecular orbital picture of Ag based halide double perovskites where Na replaces Ag involving B site cation higher energy levels of (Na)- {s, p}- Cl(p), so they do not contribute in lowest band formation. In both the cases Fermi level is denoted by E_F above and below which the CBM and VBM exists respectively. Reprinted from reference⁶¹ with permission. Copyright © 2024, American Chemical Society.

In the above band structures, the VBM and CBM are dominated by Ag (d and s orbitals), Bi/Sb and In (s and p orbitals) respectively causing the transition between $d \rightarrow s$, $s \rightarrow p$ orbitals appearing as the first transition in absorption spectra of these double perovskites.^{62, 63} Na (s, p) orbitals being very much deep seated in both VBM and CBM does not contribute in the band edges. Thereby for Bi^{3+} and Sb^{3+} (ns^2 ions) based double perovskites have allowed $s \rightarrow p$ ($ns^2 \rightarrow ns^1np^1$) transition as the first absorption in BiCl_6^{3-} or SbCl_6^{3-} moiety.^{63, 64} Indium in +3 state having d^{10} configuration,

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shows poor absorption in InCl_6^{3-} moiety. In Ag^+ based double perovskites Ag orbitals hybridizes with Bi/Sb/In. The ns^2 ions like $\text{Bi}^{3+}/\text{Sb}^{3+}$, are well known for allowed $s \rightarrow p$ transition, similarly Ag^+ involves d and s orbitals in band edges improving the band edge transition, while In^{3+} shows forbidden transition having d^{10} configuration showing poor absorption.

The ns^2 ions, $\text{Bi}^{3+}/\text{Sb}^{3+}$, also transition metal like Ag^+ with good absorption, shows luminescence when doped in some percentages to other hosts like $\text{Cs}_2\text{NaInCl}_6$,⁶⁵ Cs_2ZrCl_6 ,⁶⁶ etc due to the de-excitation of electron from $np \rightarrow ns$ orbital radiatively.⁶⁶ In that case these ions act like the luminescence centers.⁶⁴

Interestingly, when these ions become a part of host itself, they do not act as single luminescence center, rather their emission quenches in presence of too many luminescence centers due to the effect called “concentration quenching.” Due to lower concentration or dilution of luminescence centers the same ions emit when doped in a small fraction in suitable hosts. As a result, Bi^{3+} doped $\text{Cs}_2\text{NaNCl}_6$ shows emission due to de-excitation of Bi^{3+} from $ns^1np^1 \rightarrow ns^2$.⁶⁵

The composition of our interest to understand phase transition effect on photoluminescence property, among the above mentioned possibilities is, $\text{Cs}_2\text{NaBiCl}_6$, as it undergoes a temperature dependent phase transition from cubic to tetragonal, as found by Pelle et al. back in 1984.⁵⁸ But as discussed above, the composition itself does not emit light upon photoexcitation, to probe the phase transition we need to incorporate a luminescence center. Also, it is yet to understand that whether the surrounding local structure of dopant’s octahedra changes due to global structural change or not.

1.9 Choice of luminescence center

This thesis aims not to introduce a new emission channel out of many already existing in literature or for practical application in light emitting diodes, but the main interest lies in the local structural or photophysical change of dopant driven by global structural change of host by probing photo physics of dopant. Usually transition metals or lanthanides or actinides are known to be used as dopant for their well-known variable emission in wide range starting from visible to near infrared (NIR) region depending on the surroundings like ligands, coordination number, symmetry etc. For

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example, Mn^{2+} (Group 7, d-block transition metal), shows orange to red coloured emission in six coordinated octahedral environment but emits green color in tetrahedral coordination.⁶⁷⁻⁶⁹ The lanthanides and actinides despite showing emission are not expected to respond to any changes in surrounding locally or globally. Because lanthanides and actinides show emission due to transition between inner core f orbitals. The transition metal induced emissions in six coordination with Cl^- at room temperature are listed below.

Table 1.1: d-block elements showing $d-d$ transition specifically when doped in halide perovskite and emission range in six coordination.

Emissive d -block elements (ions)	Crystal field	Emissive excited state $\rightarrow$ ground state configuration	Emission wavelength (range)	References
$\text{Cr}^{3+} (d^3)$	Low	${}^4\text{T}_{2g} \rightarrow {}^4\text{A}_{1g}$	800-1300 nm	^{70, 71}
$\text{Mn}^{2+} (d^5)$	Low	${}^4\text{T}_{1g} \rightarrow {}^6\text{A}_{1g}$	550-650 nm	⁷²
$\text{Mo}^{3+} (d^3)$	High	${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$	1080-1100 nm	⁷³

Among many, a few d -block elements are found to show a separate emission from host when doped in six coordinated halide perovskites specifically like listed in table 1.1. Because of the very much dependence of the transition metal on the ligands or geometry, it is important to categorize under very precise environment. For example, the listed elements' emission wavelength may vary from Cl to Br to I or octahedra to tetrahedra. Out of the three Mn^{2+} is very doping friendly and has been extensively used as dopant for broad emission in visible region as listed in the references. During transition in Mn^{2+} there occur transition of electron one d -orbital to another making the configurational change. The configurations corresponding to ground and excited state are shown in Figure 1.15.

In case of Mn^{2+} the transition of one electron occurs from e_g to t_{2g} and pairs up. The energy of the excited state is higher mainly due to the pairing energy of two electron in t_{2g} in excited state (E.S.) in Figure 1.15. This transition energy corresponds to Δ_o . But in case of Mo^{3+} the transition happens within the t_{2g} orbital itself just by

changing a spin and the overall configuration in t_{2g} does not change. So, in case of Mn^{2+} emission, the transition is inter-configurational but in Mo^{3+} the transition is intra-configurational as also obtained in other hosts already explored earlier.^{70, 74-76} For our understanding, we have chosen Mn^{2+} and Mo^{3+} as the probing dopant for phase transition in $Cs_2NaBiCl_6$. Because i) Cr^{3+} is difficult to dope in solution phase synthesis⁷⁰ as shown in Chapter 2 and ii) in presence of Cl, Cr^{3+} shows similar inter-configurational broad emission like Mn^{2+} in NIR region having low crystal field.⁷⁰

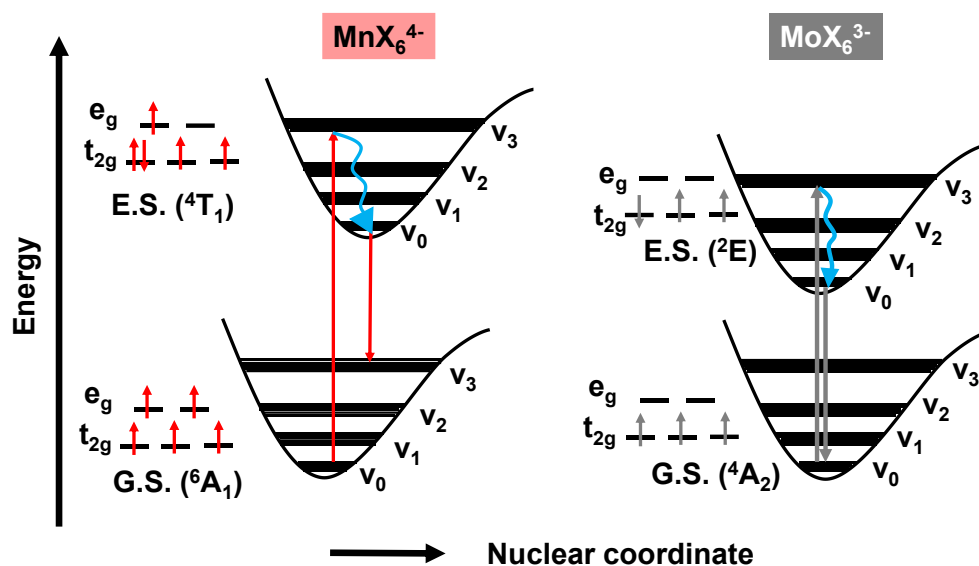


Figure 1.15: Quantitative schematic representation of emission process of Mn^{2+} (d^5) and Mo^{3+} (d^3) in octahedral symmetry giving broad (inter-configurational) and sharp (intra-configurational) emission respectively.

Intra-configurational transitions are usually found to be broad in nature while inter-configurational transitions are found to be very sharp in nature depending on their interaction with the lattice. Even, the different intra- and inter-configurational transitions from the same metal show broad and sharp features. For example, $[Mn(H_2O)_6]^{2+}$ shows inter- and intra-configurational transitions (absorption) to different electronic levels from the ground state; the corresponding absorption feature varies from broad to sharp depending on whether the transition is inter- or intra-configurational in nature.⁷⁷ It is found that the inter-configurational transition is so perturbed by the lattice vibrations (as shown by blue curved arrows in Figure 1.15) that the minute changes in bond-lengths due to phase transition from cubic to tetragonal are suppressed in Mn^{2+} when doped in $Cs_2NaBiCl_6$. But for the intra-configurational transition in Mo^{3+} , the transition does not get much perturbed by the lattice vibrations and responds to the temperature-dependent phase transition in $Cs_2NaBiCl_6$.

1.10 Scope of The Thesis

Halide perovskites often change their crystal structure based on external condition like temperature and pressure. This structural phase transition may lead to changes in their inherent semiconducting properties like bandgap, luminescence, and carrier mobility. Another way of tailoring properties is by lattice doping. For example, dopants like Mn^{2+} and Mo^{3+} introduces interesting luminescence properties. The emphasis of this thesis work is to study the correlation between structural phase transition, doping, and luminescence in halide perovskites. The work has been extended for both macroscopic bulk crystals and NCs.

We started with $\text{Cs}_2\text{NaBiCl}_6$ double perovskite that is known to undergo a temperature dependent phase change from cubic ($Fm-3m$) to tetragonal ($I4/mmm$), below 110 K as shown in Figure 1.16a. Mn^{2+} and Mo^{3+} ions are doped as luminescence centers in $\text{Cs}_2\text{NaBiCl}_6$. Doping Mn^{2+} ions leads to a broad orange-red coloured emission owing to its $d-d$ electronic transition (left side orange coloured emission spectra in Figure 1.16b). It has caught our attention that whether i) doping a small percentage of dopant can change the phase transition property of $\text{Cs}_2\text{NaBiCl}_6$ or not, ii) whether the local dopant's surrounding octahedral geometry changes with the global structural change from cubic to tetragonal. Along with that, since, the broad emission is dependent on ligands and geometry around the Mn^{2+} ions, whether the emission arising from dopant octahedra gets affected by structural phase transition or not. Because upon changing the ligands, from Cl, to Br to I, Mn emission varies not significantly but noticeable from orange to red region. So, it was expected that upon changing the geometry from cubic to tetragonal the local environment can be affected. This effect can be monitored by photoluminescence experiment where the photoluminescence should come from the dopant center. But Mn^{2+} emission being hampered by lattice vibrations, are much broader in nature. Also, the cubic to tetragonal change is a very minimal, only by one axis elongation. So, in difference to Mn^{2+} , another dopant is chosen which is sensitive towards the ligands and geometry, but having narrower emission is more sensitive towards minimal local environmental change. The Mo^{3+} dopants show a sharp intra-configurational NIR emission (~ 1095 nm, as shown in right side gray colored emission spectra in Figure 1.16b), thereby it was expected Mo^{3+} may show different behavior around phase transition temperature than the inter-configurational broad emission of Mn^{2+} .

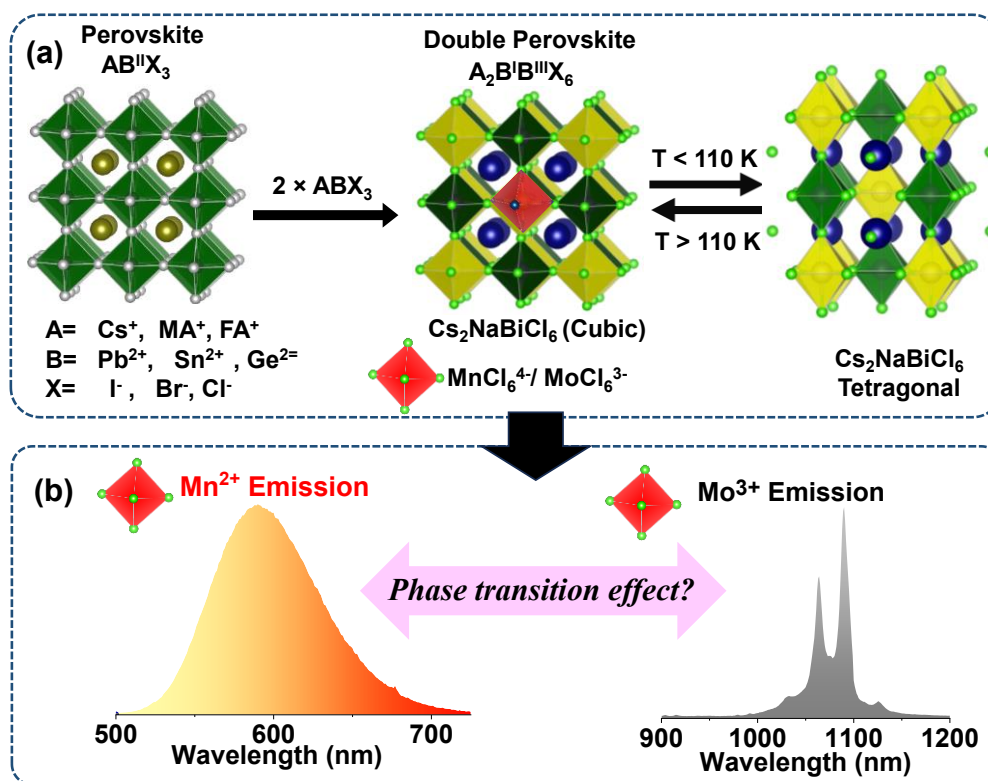


Figure 1.16: (a) Evolution of double perovskite from conventional perovskite structure and phase transition of $Cs_2NaBiCl_6$ perovskite with temperature, red octahedra denotes the doping of foreign element like Mn^{2+}/Mo^{3+} in $Cs_2NaBiCl_6$ (b) Emission introduced by Mn^{2+} (orange, left) and Mo^{3+} (gray, right) in $Cs_2NaBiCl_6$ in octahedral coordination.

Furthermore, the structural phase transition might change for NCs, because of the higher contribution of the surface energy. Indeed, our data do not show the signature of the cubic to tetragonal transition of $Cs_2NaBiCl_6$ NCs ~ 110 K, unlike their bulk counterpart as shown in Figure 1.17a.

Lastly, we prepared colloidal methylammonium lead bromide ($MAPbBr_3$) NCs with different shapes—nanocubes and nanoplatelets. The size- and shape-dependent optical properties were studied. At lower synthesis temperature nanoplatelets form and at higher synthesis temperature nanocubes form. The nanoplatelets, along with their capping ligands, behave more like pseudo two-dimensional perovskites. Here the crystal structure remains the same still the electronic band structure varies based on the shape of NCs due to quantum confinement introduction which alter the optical property of nanoplate and nanocubes. Also it was observed depending on the shape the nanocrystals show different tendency to stack with one another when deposited on substrates.

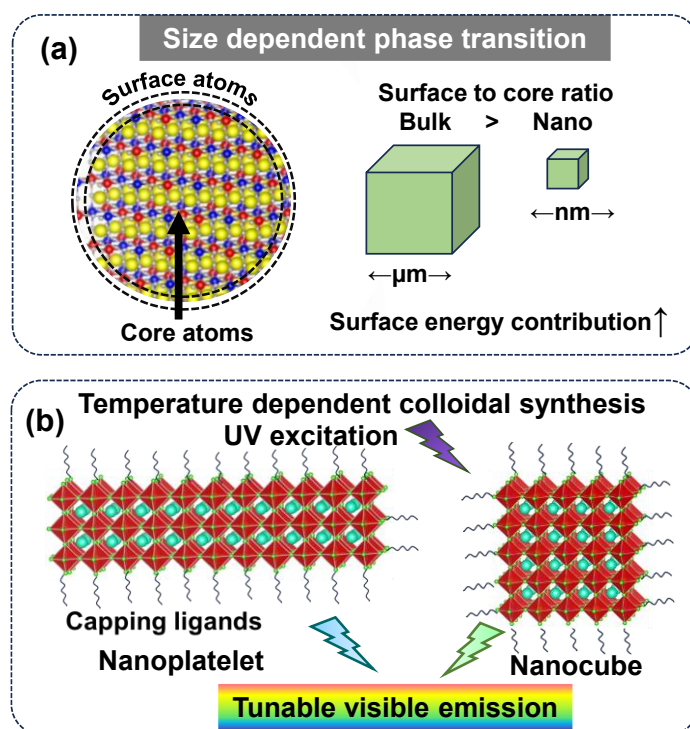


Figure 1.17: (a) Different phase transition behavior depending on crystal size from bulk to nano, due to huge different surface energy contribution (b) Different optical properties (as obtained from different colors) arising from MAPbBr₃ nanoplatelets with variable thickness and nanocubes covering variable emission wavelength in visible region, obtained by temperature dependent colloidal synthesis.

Overall, the thesis work provides insights into the interplay between dopants, dimensionality, and phase stability of halide perovskites for optoelectronic applications. The category of transitions that respond to crystal structure while some do not are probed by doping, as well as crystal size change itself alters the phase transition property. Lastly, the different shape of same compositions alters the luminescence property which has been probed by synthesizing different shaped NCs having the same phase.

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Chapter 2A

Unveiling Temperature-Induced Structural Phase Transition and Luminescence in Mn²⁺-Doped Cs₂NaBiCl₆ Double Perovskite

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Declaration:

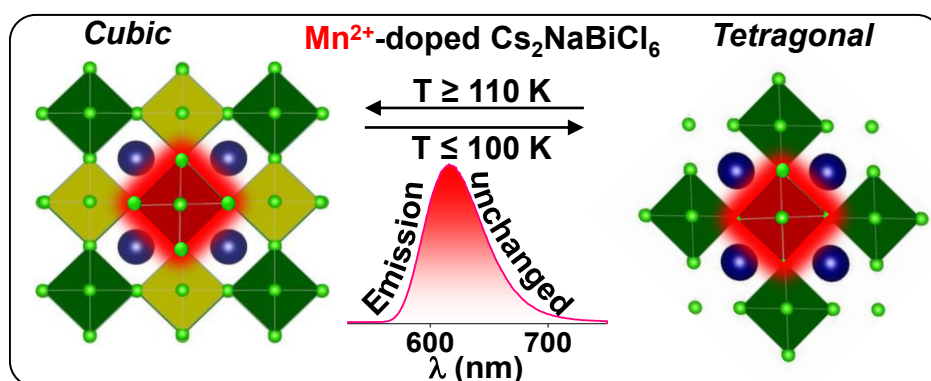
Low temperature powder X-Ray diffraction analysis has been done by Dr. Maksim S. Molokeev. Dr. Sajid Saikia helped in sample preparation and measurements.

Unveiling Temperature-Induced Structural Phase Transition and Luminescence in Mn^{2+} -Doped $\text{Cs}_2\text{NaBiCl}_6$ Double Perovskite

Abstract

Halide double perovskites like $\text{Cs}_2\text{NaBiCl}_6$ are good host materials for luminescent dopants like Mn^{2+} . The nature of photoluminescence (PL) depends on the local structure around the dopant ion, and doping may sometimes influence the global structure of the host. Here, we unveil the correlation between the temperature-induced (global) structural phase transition of Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ with the local structure and PL of the Mn^{2+} dopant. X-ray diffraction analysis shows Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ is in a cubic ($Fm\bar{3}m$) phase between 300 and 110 K, below which the phase changes to tetragonal ($I4/mmm$), which persists at least until 15 K. The small ($\sim 1\%$) doping amount does not alter the phase transition behavior of $\text{Cs}_2\text{NaBiCl}_6$. Importantly, the phase transition does not influence the Mn^{2+} d-electron PL. The PL peak energy, intensity, spectral width, and lifetime do not show any signature of the phase transition between 300–6 K. The hyperfine splitting in temperature-dependent electron paramagnetic spectra of Mn^{2+} ions also remain unchanged across the phase transition. These results suggest that the global structural phase transition of the host does not influence the local structure and emission property of the dopant Mn^{2+} ion. This structure–property insight might be explored for other transition-metal- and lanthanide-doped halide double perovskites as well. The stability of dopant emission regardless of the structural phase transition bodes well for their potential applications in phosphor-converted light emitting diodes.

Graphical Abstract



2A.1 Introduction

Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ double perovskites emit red light, indicating their potential for phosphor-converted light emitting diode (pc-LED) applications.^{1, 2} Interestingly, such double perovskites often show a temperature-dependent structural phase transition. Can Mn^{2+} doping influence the phase transition? On the other hand, does the structural phase transition influence the luminescence properties of Mn^{2+} dopants? Here, we address these questions, by employing structural and photoluminescence (PL) measurements in the temperature range of 7–300 K. This insight into the structure–property relationship is critical for advancing Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$, and other doped halide double perovskites, for their optoelectronic applications.

Lead halide-based perovskites show excellent properties relevant for solar cells, LEDs, photodetectors, chiral optoelectronics, and quantum light emitters.^{3–13} These findings prompted researchers to explore environmentally benign Pb-free halide perovskites.^{14–17} Consequently, halide-based double perovskites with the generic formula $\text{Cs}_2\text{BB}'\text{X}_6$ ($\text{B} = \text{Ag}, \text{Na}$; $\text{B}' = \text{Bi}, \text{In}, \text{Sb}$; $\text{X} = \text{Cl}, \text{Br}$) emerged as a versatile class of material, that retain the three-dimensional (3D) perovskite crystal structure, as shown in Figure 2A.1.

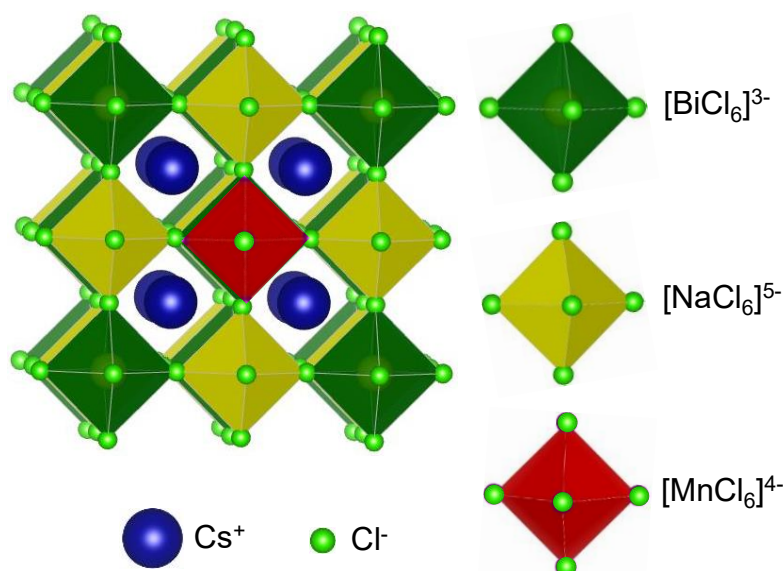


Figure 2A.1: Schematics of Mn^{2+} doped in $\text{Cs}_2\text{NaBiCl}_6$ double perovskite lattice at room temperature.

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But the halide double perovskites have either a wide band gap and/or a forbidden optical transition across the band gap, limiting their optical and optoelectronic properties. To overcome the issue, different doping strategies have been employed, which can introduce both light emitting and absorbing states in the midgap region.¹⁸ Mn²⁺ doping in Cs₂AgInCl₆ double perovskite emitting the red light is one of the first reports of doping in halide double perovskites.¹⁹ Subsequently, dopants like Bi³⁺, Sb³⁺, Te⁴⁺, Cr³⁺, Yb³⁺, and Er³⁺ have been doped in different halide double perovskites, showing interesting dopant emissions in both visible and short-wave infrared (SWIR) region.^{18, 20-24} Some of the doped halide perovskites exhibit high thermal stability, making them serious candidates for pc-LED applications, though efficient electroluminescence still remains a challenge because of the poor charge transport in the hosts.^{23, 24}

The global and local structure around the dopant center control the optical and optoelectronic properties. Most of the perovskites and double perovskites show structural phase transitions with variation in temperature and pressure.²⁵⁻²⁹ For example, Cs₂NaBiCl₆ crystallizes in the cubic *Fm-3m* space group at room temperature (Figure 2A.3a) and converts to the tetragonal *I4/mmm* phase below 110 K.³⁰ Such phase transitions might influence the dopant emission that is sensitive to the crystal field around the dopant ion. Both peak energy and lifetime of Mn²⁺ emission depend on the ligand field around the Mn²⁺ ion.^{31, 32} Also, it has been shown that a dopant ion can alter the phase transition behavior of halide perovskites. For example, doping of Mn²⁺ or Bi³⁺ can stabilize the black perovskite phase of CsPbI₃ at room temperature, which is otherwise unstable at room temperature.³³⁻³⁵ Such studies of whether Mn²⁺ doping can alter the phase transition of halide double perovskites like Cs₂NaBiCl₆ are not available in the literature. There are reports of temperature-dependent photoluminescence of Mn²⁺ ions doped inside halide perovskite and double perovskite systems,^{36, 37} but those temperature-dependent optical studies have not been correlated with structural phase transition.

Our powder X-ray diffraction (XRD) data of Mn²⁺-doped Cs₂NaBiCl₆ show a cubic (*Fm-3m*) (Figure 2A.3b) to tetragonal (*I4/mmm*) phase transition below 110 K, similar to the undoped crystal. In the tetragonal phase, the *c*-axis elongates, distorting the [BiCl₆]³⁻ octahedron (elongating the Bi–Cl bond along the *c*-axis). Such distortion

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might influence the Mn²⁺ *d*-electrons emission, since Mn²⁺ prefers² to substitute the Bi³⁺ site in the Cs₂NaBiCl₆ lattice. But the observed optical emission of Mn²⁺-*d*-electrons remains unperturbed by the structural phase transition. To probe the local structure around the Mn²⁺ ion, we employed temperature-dependent electron paramagnetic resonance (EPR) spectroscopy. The EPR hyperfine splitting energy of Mn²⁺ in both the cubic and tetragonal phases remain the same at 9 mT. Overall, the PL and EPR data suggest that the local structure around the Mn²⁺ ion does not change significantly, in spite of the global phase transition observed by the XRD data.

2A.2 Experimental Section

2A.2.1 Chemicals

Cesium chloride (CsCl, 99.9%), sodium chloride (NaCl, 99.999%), bismuth chloride (BiCl₃, 99.99%), manganese chloride (MnCl₂, 99.99%) and hydrochloric acid (HCl, aqueous 37% w/w) are purchased from Sigma Aldrich chemicals. Ethanol (≥99.80%) is purchased from Rankem. All of the chemicals are used without any further purification.

2A.2.2 Synthesis of Mn²⁺ Doped Cs₂NaBiCl₆

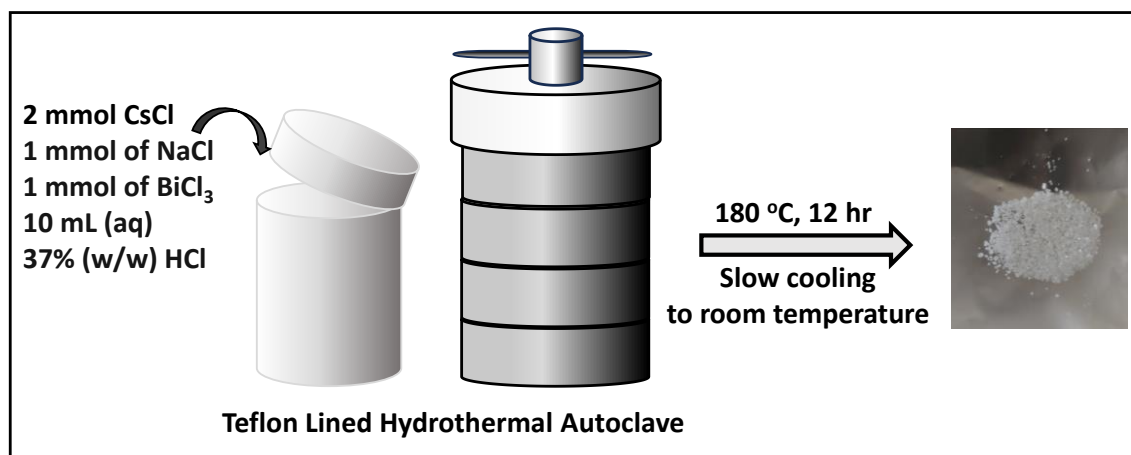


Figure 2A.2: Schematic of synthesis undoped and Mn²⁺ doped Cs₂NaBiCl₆.

Figure 2A.2 represents the reaction procedure using hydrothermal method. The reaction happens in a closed medium so with increased pressure at higher temperature the elevation of boiling point of the solvent happens, so that the solvent for example Hydrochloric acid (HCl) here, can be heated at a much higher temperature

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than its boiling point at atmospheric pressure. At higher temperature and pressure solubility of the precursor also increases. Then slowly cooling the reaction mixture to room temperature gives good quality and larger sized crystals as compared to acid precipitation methods which is often performed at a temperature below solvent's boiling point at atmospheric pressure.

Cs₂NaBiCl₆ double perovskite is synthesized by modifying the hydrothermal method that was reported earlier.¹⁸ 2 mmol of CsCl, 1 mmol of NaCl, 1 mmol of BiCl₃ and 10 mL of aqueous solution of 37% (w/w) HCl are taken in a 25 mL Teflon container, which is then packed inside an autoclave. The reaction mixture is heated at 180 °C for 12 h inside an oven. Then it is naturally cooled to room temperature. The obtained crystals are washed with ethanol, dried in vacuum for 3 h, and then stored in glass vials under ambient conditions for further study. For the synthesis of Mn²⁺-doped Cs₂NaBiCl₆, the method remains the same as that of the undoped sample, with the only change being the addition of MnCl₂ in the autoclave.

2A.2.3 Characterization

Elemental analysis of the product is carried out by employing inductively coupled plasma atomic emission spectroscopy (ICP-AES) using SPECTRO Analytical Instruments GmbH, Germany, ARCOS, Simultaneous ICP Spectrometer. The Mn²⁺ dopant % = $100 \times [\text{Mn}] / ([\text{Na}] + [\text{Bi}] + [\text{Mn}])$, where [Na], [Bi] and [Mn] are concentrations of Na, Bi, and Mn obtained from ICP-AES measurements, respectively. Powder XRD patterns are measured in a wide temperature range of 15 to 300 K using a Bruker D8Advance X-ray diffraction machine equipped with Cu K α (1.54 Å) radiation and a 1D strip detector. The step size of 2 θ was 0.016°, and the counting time was 2 s per step. Rietveld analysis of Powder XRD patterns are done by using TOPAS 4.2 software.³⁸ EPR measurements are performed at different temperatures (300–85 K) using JON Bruker Bio Spin connected to Bruker EMX plus spectrometer with a radio wave source (9.737205 GHz, X-band).

UV–visible diffuse reflectance spectra are measured using a Shimadzu UV-3600 plus UV–vis-NIR spectrometer. The diffused reflectance spectra are then converted to absorbance by using the Kubelka–Munk transformation following eq (1):

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$$F(R) = \left(\frac{\alpha}{S}\right) = \frac{(1-R)^2}{2R} \quad (1)$$

where $F(R)$ is the Kubelka–Munk function, R is the reflectance, α is the absorption coefficient, and S is the scattering factor.³⁹ For PL measurements at room temperature, the powder samples are taken between two quartz plates, one with a fixed groove dimension to maintain a similar amount of powder used for all measurements. All the PL, PL excitation (PLE), and PL decay dynamics (time-correlated single-photon counting) are measured using an Edinburgh FLS980 instrument. The samples are excited using a xenon lamp for PL and PLE measurements unless otherwise mentioned. For PL lifetime measurements in the millisecond (ms) time range, a microsecond flash lamp of Edinburgh Photonics (uF920H) was used to excite the samples. Temperature-dependent PL, PLE, and PL decay measurements are carried out in the same Edinburgh instrument coupled with a cryostat. A thin layer of the powdered samples is placed between two sapphire plates and mounted by sandwiching between two gold-coated copper holders. The samples are then inserted in a closed cycle helium cryostat from Advanced Research Systems, which is attached with a Lake Shore 335 temperature controller to achieve the desired temperatures in the range of 6 to 300 K. Experimental PL decay profiles are fitted using biexponential decay functions shown in eq (2):

$$I_t = I_o + \sum_{n=1}^2 A_n e^{-\frac{t}{\tau_n}} \quad (2)$$

Where I_t is the PL counts at any time t , I_o is the offset, and τ_n is PL lifetime with contribution A_n . The average PL lifetime (τ_{avg}) for biexponential decay is calculated using equation (3)

$$\tau_{avg} = \frac{\sum_{n=1}^2 A_n \tau_n^2}{\sum_{n=1}^2 A_n \tau_n} \quad (3)$$

The dimensionless Huang–Rhys parameter (S), which is a measure of electron–phonon coupling, can be estimated from the temperature(T)-dependent variation of full-width-at-half-maxima (FWHM) of PL spectra, following eq (4), where $\hbar$ is the Planck constant, ω_{ph} is phonon frequency, and k_B is Boltzmann constant.

$$FWHM = 2.36\sqrt{S}\hbar\omega_{ph}\sqrt{\coth\left(\frac{\hbar\omega_{ph}}{2k_B T}\right)} \quad (4)$$

2A.2.4 Methodology to Compare the PL Intensity

For comparison of PL intensity, 20 mg of the powdered sample was thoroughly mixed with 120 mg BaSO_4 powder. BaSO_4 does not interfere with excitation and visible emission of Mn^{2+} of the sample. So, the role of BaSO_4 is to dilute the sample, similar to a solvent in a colloidal dispersion. For every measurement, equal amount mixed (sample + BaSO_4) powder is taken in a quartz sample holder which has a definite size groove in it and PL spectra are recorded at multiple spots of the mixed powder. Then the average out spectra are used for comparison.

2A.3 Results and Discussion

2A.3.1 Mn^{2+} Doping

The powder XRD pattern of the undoped $\text{Cs}_2\text{NaBiCl}_6$ at room temperature and the corresponding Rietveld refinement are shown in Figure 2A.3a. The sample crystallizes in a face centered cubic $Fm-3m$ space group, with the lattice parameter of $10.847 \pm 0.001 \text{ \AA}$, which is in good agreement with the previous report.⁴⁰ Refinements are stable and give low R-factors.

Dopant (Mn^{2+}) percentages are determined by ICP-AES and presented in Table 2.2. ICP-MS data provides the complete elemental analysis. In spite of using high amounts of Mn^{2+} precursor, only a small fraction of Mn^{2+} ions is present in the product.

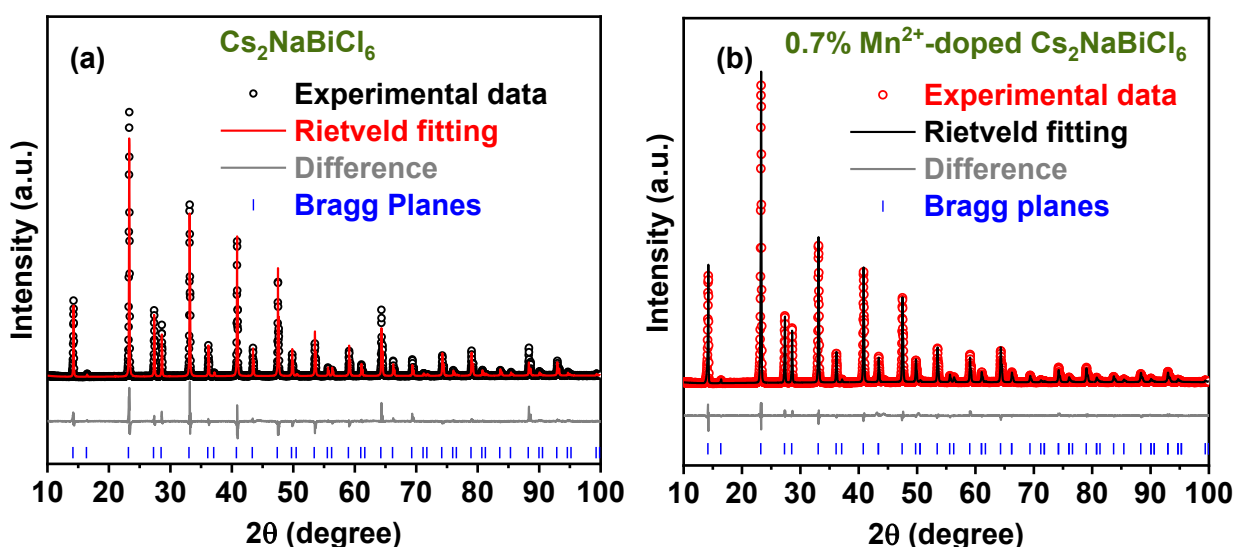


Figure 2A.3: Rietveld fitting of powder XRD patterns of (a) undoped and (b) 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ at room temperature.

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Then considering the undoped sample as the standard one, we performed the Rietveld analysis of the Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ at room temperature, as shown in Figure 2A.3b. 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ also crystallizes in the $Fm-3m$ space group with a lattice parameter of 10.832 ± 0.001 Å, similar to that of the undoped sample. The parameters are listed in Table 2A.1.

Table 2A.1: Main parameters of processing and refinement of powder XRD patterns of undoped and 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ at room temperature. Both samples crystallize in the same cubic space group of $Fm-3m$.

Cell parameters, a (Å), Cell Volume, V (Å ³)		R_{wp} , R_p , R_B , χ^2	
Undoped	0.7% doped	Undoped	0.7% doped
$a = 10.84700(0)$ $V = 1276.23(5)$	$a = 10.83284(15)$, $V = 1271.24(5)$	6.23, 4.76, 4.88, 2.08	8.66, 6.01, 2.87, 2.06

The percentage of Mn^{2+} doping is varied by changing the concentration of the Mn^{2+} precursor in the reaction mixture (Table 2A.2). Powder XRD patterns in Figure 2A.4a show phase-pure samples up to 1.3% of Mn^{2+} doping, without the appearance of any extra peak. However, further increase in doping concentration to 6.2% leads to the appearance of additional impurity peaks, as shown in Figure 2A.5, so we restrict our study up to 1.3% Mn^{2+} -doping, which is expected to be sufficient to yield the maximum Mn^{2+} luminescence.¹ This may be because the difference in the oxidation state and ionic radius of Mn^{2+} compared to those of host B-site cations Bi^{3+} and Na^+ reduces the doping efficacy. The ionic radius of the high-spin Mn^{2+} ion in octahedral coordination is 0.83 Å, which is significantly smaller than both Na^+ (1.02 Å) and Bi^{3+} (1.03 Å) in octahedral coordination.⁴¹ It was suggested that the Mn^{2+} dopants substitute Bi^{3+} sites in $\text{Cs}_2\text{NaBiCl}_6$,² so incorporation of Mn^{2+} into the lattice $\text{Cs}_2\text{NaBiCl}_6$ is supposed to contract the unit cell, reducing the interplanar distance. Indeed, Figure 2A.4b shows a systematic shift in XRD peaks toward higher 2θ values indicating a decrease in interplanar distances with increasing the Mn^{2+} concentration.

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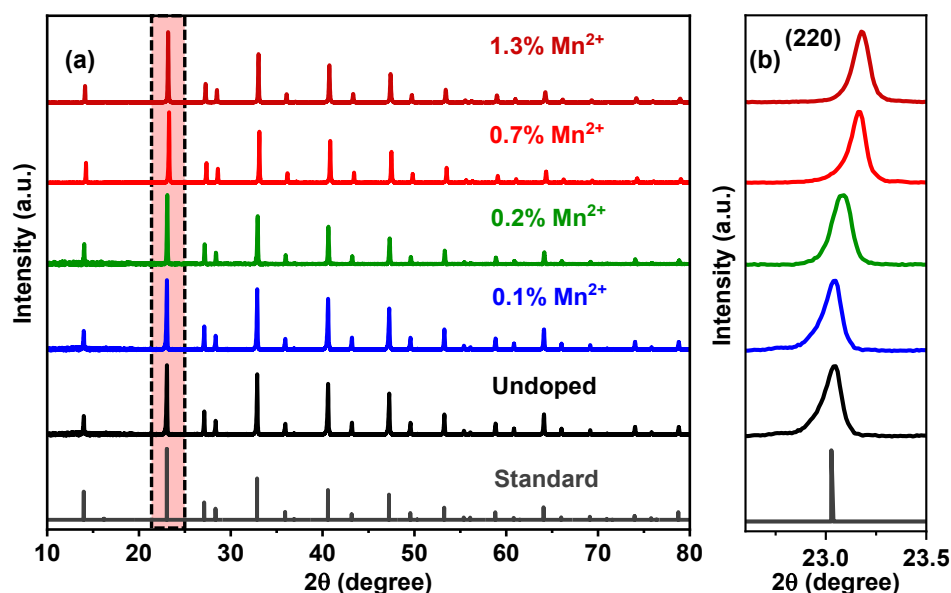


Figure 2A.4: (a) Powder XRD patterns of Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ with different dopant concentrations along with the reference pattern of $\text{Cs}_2\text{NaBiCl}_6$ in the cubic phase with space group $Fm-3m$. (b) Magnified view of the XRD patterns.

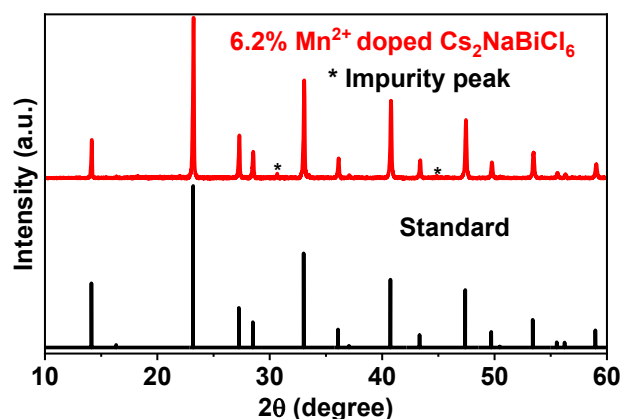


Figure 2A.5: Room temperature powder XRD pattern of 6.2% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ compared with reference pattern of $\text{Cs}_2\text{NaBiCl}_6$ in cubic phase ($Fm-3m$). Minor impurity peaks are observed as indicated by * in the figure.

Table 2A.2: Molar feed ration of Bi, Na, and Mn in precursor, with that in the product obtained from ICP-AES elemental analysis.

Molar ratio of precursor Bi : Na : Mn	Molar ratio obtained from ICP-AES analysis of product = Bi : Na : Mn	Mn^{2+} dopant % in product
1 : 1 : 0	1 : 1 : 0	0
1 : 1 : 0.1	1 : 1 : 0.002	0.1%
1 : 1 : 0.2	1 : 1 : 0.004	0.2%
1 : 1 : 0.35	1 : 1 : 0.013	0.7%
1 : 1 : 0.5	1 : 1 : 0.026	1.3%

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The Mn²⁺ dopant % = $100 \times [\text{Mn}] / ([\text{Na}] + [\text{Bi}] + [\text{Mn}])$, where [Na], [Bi] and [Mn] are concentrations of Na, Bi, and Mn obtained from ICP-AES analysis, respectively.

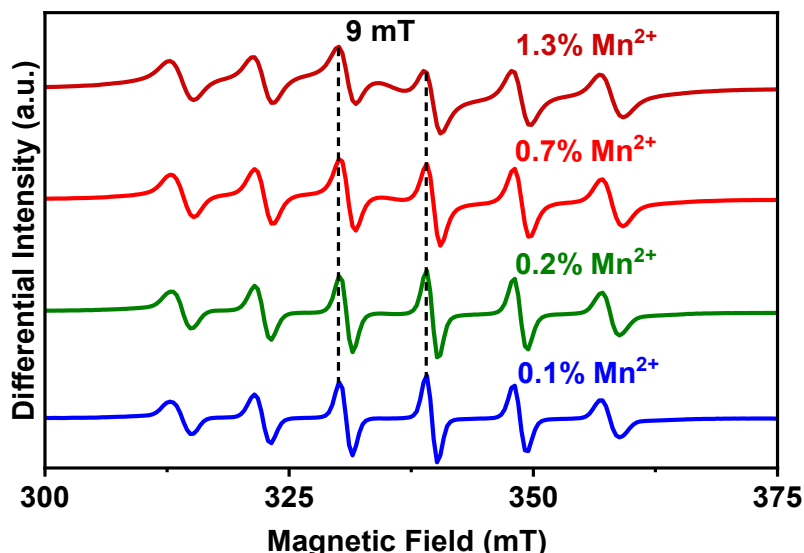


Figure 2A.6: EPR spectra of Mn²⁺-doped Cs₂NaBiCl₆ with different dopant concentrations. All the data shown in this figure are measured at room temperature.

While XRD shows the averaged out structural information on unit cell contraction and suggests Mn²⁺ doping into the lattice, EPR spectra can provide information regarding the local structure around the Mn²⁺ dopant centers. High-spin Mn²⁺ ions have five unpaired electrons, making them EPR-active, and are known to show sextet lines because of hyperfine splitting with nuclear spin $I = 5/2$.¹⁹ Six clear peaks in EPR spectra are observed for Mn²⁺-doped Cs₂NaBiCl₆ at room temperature, as shown in Figure 2A.6. The peaks are well-resolved, suggesting that the Mn²⁺ dopants are well-separated from each other, which again supports the homogeneous distribution of Mn²⁺ into a lattice, negating the formation of any kind of clustering of Mn²⁺ species. A slight broadening of the EPR signal just started to appear at a higher dopant concentration of 1.3% due to dipole-dipole interactions between Mn²⁺ ions. The obtained value of hyperfine splitting is 9 mT with a g-factor of 1.98 for all the samples with different dopant concentrations. The results agree with the prior reports of Mn²⁺ ions incorporated in an octahedral environment of the host lattice.^{19, 42-45} The EPR data, in conjunction with the XRD data, confirm the homogeneous doping of Mn²⁺ ions in the octahedral lattice site of Cs₂NaBiCl₆.

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2A.3.2 Optical Properties of Undoped, 0.1%, 0.2%, 0.7% and 1.3% Mn^{2+} Doped $\text{Cs}_2\text{NaBiCl}_6$

Optical absorption data of Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ with different dopant concentrations are shown in Figure 2A.7a. A wide band gap of 3.28 eV (378 nm) is observed for the undoped sample, which agrees with the prior reports¹ of $\text{Cs}_2\text{NaBiCl}_6$. PL spectra of Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ are shown in Figure 2A.7b. A big change in PL is observed after Mn^{2+} doping. The undoped sample does not emit detectable emission at room temperature probably because of their indirect or wide band gap. But after Mn^{2+} doping, an emission peak appears at 595 nm, which has been assigned earlier as a $^4\text{T}_1$ to $^6\text{A}_1$ d -electron transition of Mn^{2+} ions.¹ This is a spin-and Laporte-forbidden transition. Consequently, a long average PL lifetime of 0.33 ms is observed, as shown by the PL decay data in Figure 2A.8. The intensity of the Mn^{2+} emission increases with increasing Mn^{2+} doping from 0.1% to 0.7%, but a further increase in doping concentration to 1.3% Mn^{2+} starts to show a decrease in the PL intensity. The decrease in PL intensity beyond a certain dopant concentration is often observed because the Mn^{2+} ions start interacting with each other at higher concentrations.^{1, 19}

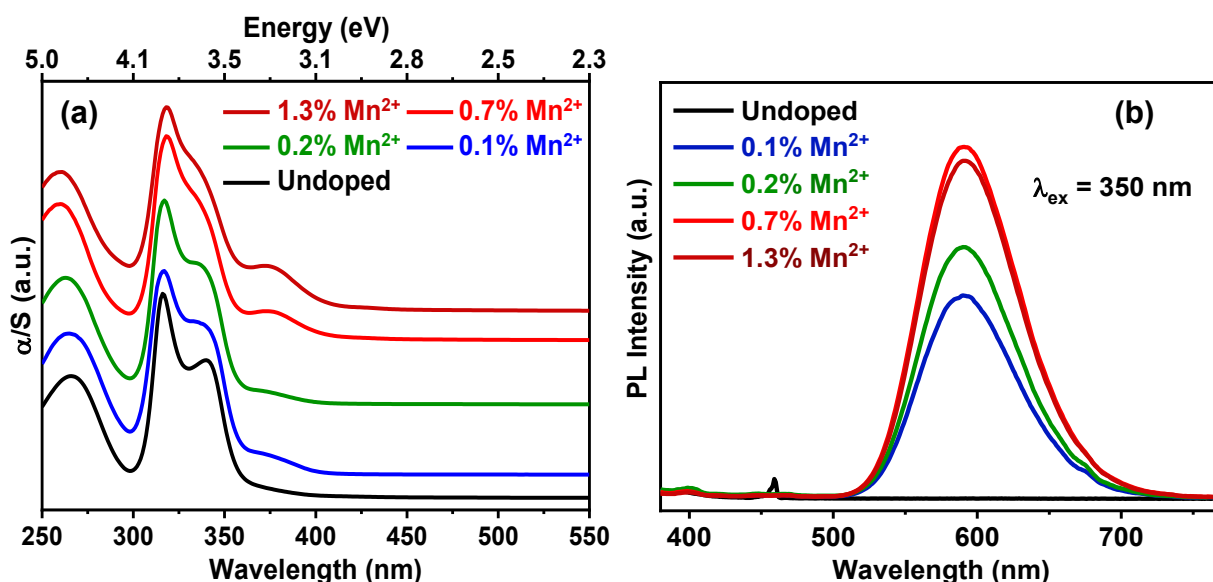


Figure 2A.7: (a) Kubelka-Munk transformed diffused reflectance spectra of Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ with dopant concentrations. The spectra are shifted vertically for clarity in presentation (b) PL spectra of Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ with different dopant concentrations. All the data shown in this figure are measured at room temperature.

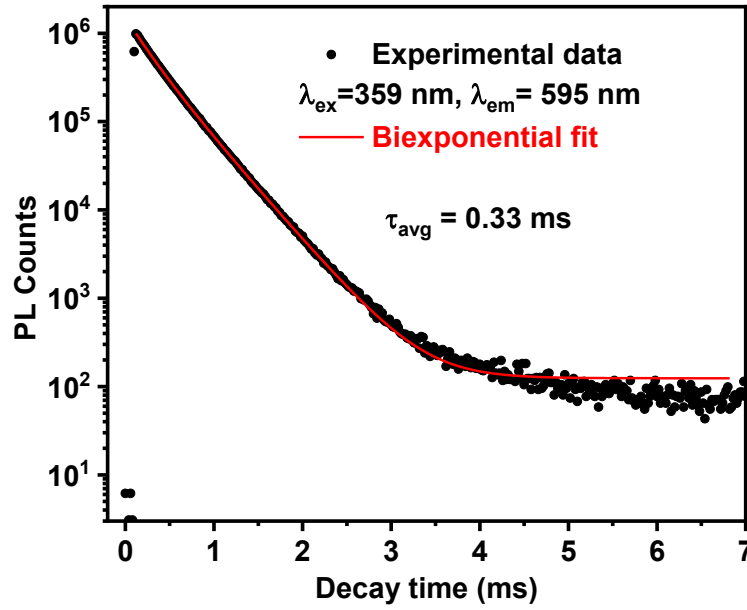


Figure 2A.8: PL decay dynamics of 0.7% Mn^{2+} -doped $Cs_2NaBiCl_6$ at 300 K. The experimental data are fitted by using a bi-exponential decay equation (eq 2).

2A.3.3 Temperature-Dependent Phase Transition

Now we discuss the temperature-dependent powder XRD patterns in the range of 15 to 300 K. The sample with 0.7% Mn^{2+} doping is chosen since it gives the highest PL intensity at room temperature (Figure 2A.7b). Figure 2A.9 shows that the XRD peaks shift slightly toward higher 2θ values with decreasing temperature from 300 to 120 K. This shift at lower temperature is usually observed because of the lattice contraction. But at 80 K, the XRD pattern changes its characteristics. For example, a single peak around 33.3° at 120K splits into two peaks at 80 K. At 120 K (and higher temperatures), the sample possesses a cubic phase with lattice parameters $a = b = c$, and therefore, interplanar distances corresponding to planes (004), (400), and (040) are the same, yielding a single peak at around 33.3° . At 80 K, the peak splits into two peaks with an lattice parameters, such as “ c ”. The c -elongation will lead to smaller 2θ values for the (004) intensity ratio of roughly 1:2. Such an observation might arise due to elongation of one of the planes, compared to (400) and (040) planes following,

$$\text{For cubic, } a = b = c \quad \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad \text{eq (5)}$$

$$\text{For tetragonal elongation, } c > a, b \quad \frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad \text{eq (6)}$$

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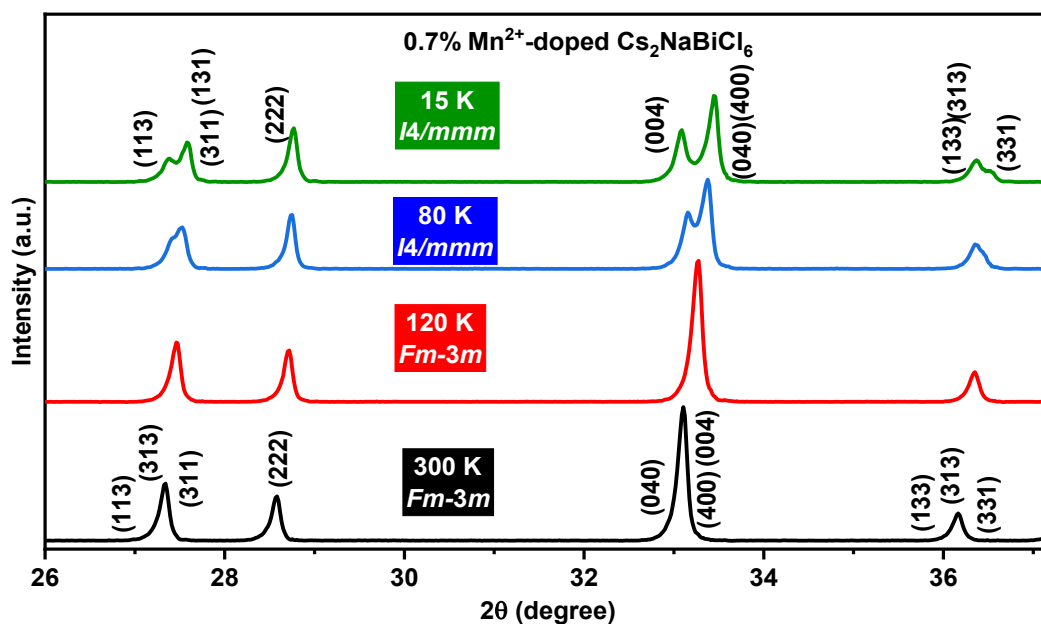


Figure 2A.9. (a) Powder XRD patterns of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ at four temperatures.

Similar temperature-dependent changes (Figure 2A.9) are also observed for (113), (131), and (311) planes. At 120 K, all three planes have the same interplanar distance resulting in a single peak at around 36.3° . But at 80 K, the probable c -axis elongation of the unit cell leads two peaks, the lower 2θ value corresponding to (133) and (313) planes (same $l = 3$), along with a peak (331) at higher 2θ and nearly half intensity. The crystal structure of 80 K is retained at lower temperatures at least until 15 K (the lowest temperature limit of our experiment). The resolution of the peak splitting increases with decreasing temperature. It is to be noted that the planes with same h , k and l values, like (222) do not split even at 15K, because elongation along any axis will not result in different interplanar distances for such planes. Overall, the data suggest a phase transition of Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ from cubic to tetragonal (c -axis elongation) lattice at lower temperatures, as was suggested earlier³⁰ for the undoped $\text{Cs}_2\text{NaBiCl}_6$.

To have a better characterization of crystal structure, we have carried out Rietveld refinement for all the powder XRD patterns of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ measured across the temperature range of 15 to 300 K. Figure 2A.10 shows the Rietveld refinement data at 15 K. A tetragonal space group of $I4/mmm$ is obtained at 15 K, in difference with the cubic $Fm-3m$ space group observed at room temperature.

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Similarly, Rietveld refinement of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ at other temperatures (15 to 300 K) are shown in Figure 2A.11 and 2A.12, along with the major refinement parameters in Table 2A.3. PXRD data at different temperatures are recorded by Srijita Banerjee and Rietveld refinement and derivation of temperature dependent parameter was done by Prof. Maksym S. Molokeev. The main bond lengths and fractional atomic coordinates at all the measured temperatures are shown in Table 2A.4. We observe a clear cubic $Fm-3m$ space group in the temperature range of 300 to 110 K, below which, in the range of 100 to 15 K, the tetragonal $I4/mmm$ phase is observed. In both temperature regions 300–110 K and 100–15 K, the crystal phases are very pure without any mixing. So, a sharp temperature-dependent phase change is observed here for the Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$.

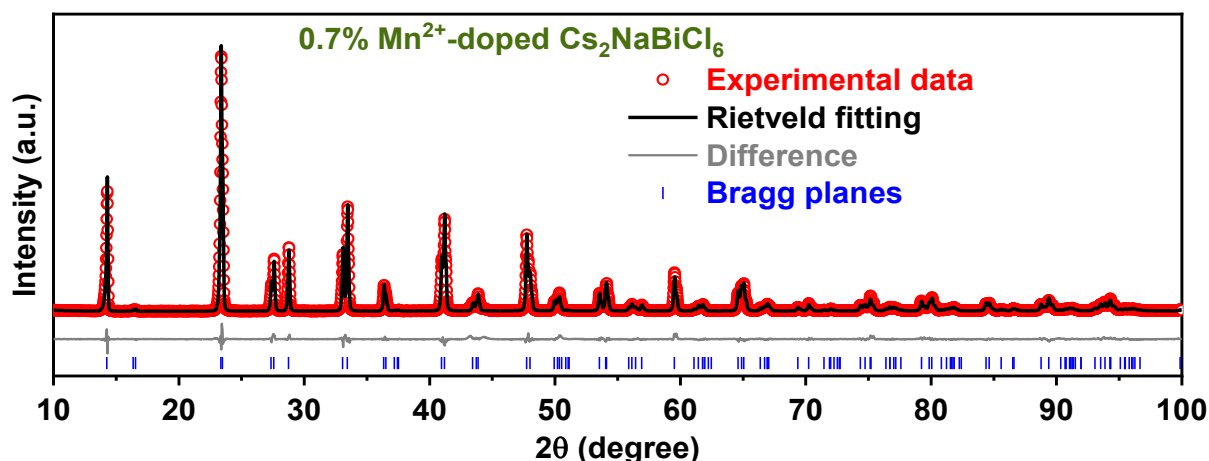


Figure 2A.10: Rietveld refinement of the XRD pattern of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ measured at 15 K.

All peaks at $T > 100$ K were indexed by cubic cell ($Fm-3m$) and all peaks at $T \leq 100$ K were indexed by tetragonal cell ($I4/mmm$) which is in line with the findings of the $\text{Cs}_2\text{NaBiCl}_6$ phase transition investigation.³⁰ Therefore, these structures³⁰ were taken as starting model for Rietveld refinement which was performed using TOPAS 4.2.³⁸ Refinements were stable and gave low R-factors (Table 2A.3-4, Figure 2A.11-12). Coordinates of atoms and main bond lengths are in Table 2A.5 and Table 2A.6 respectively. Temperature dependences of cell parameters are depicted in Figure 2 and they have similar behavior with the reference.³⁰

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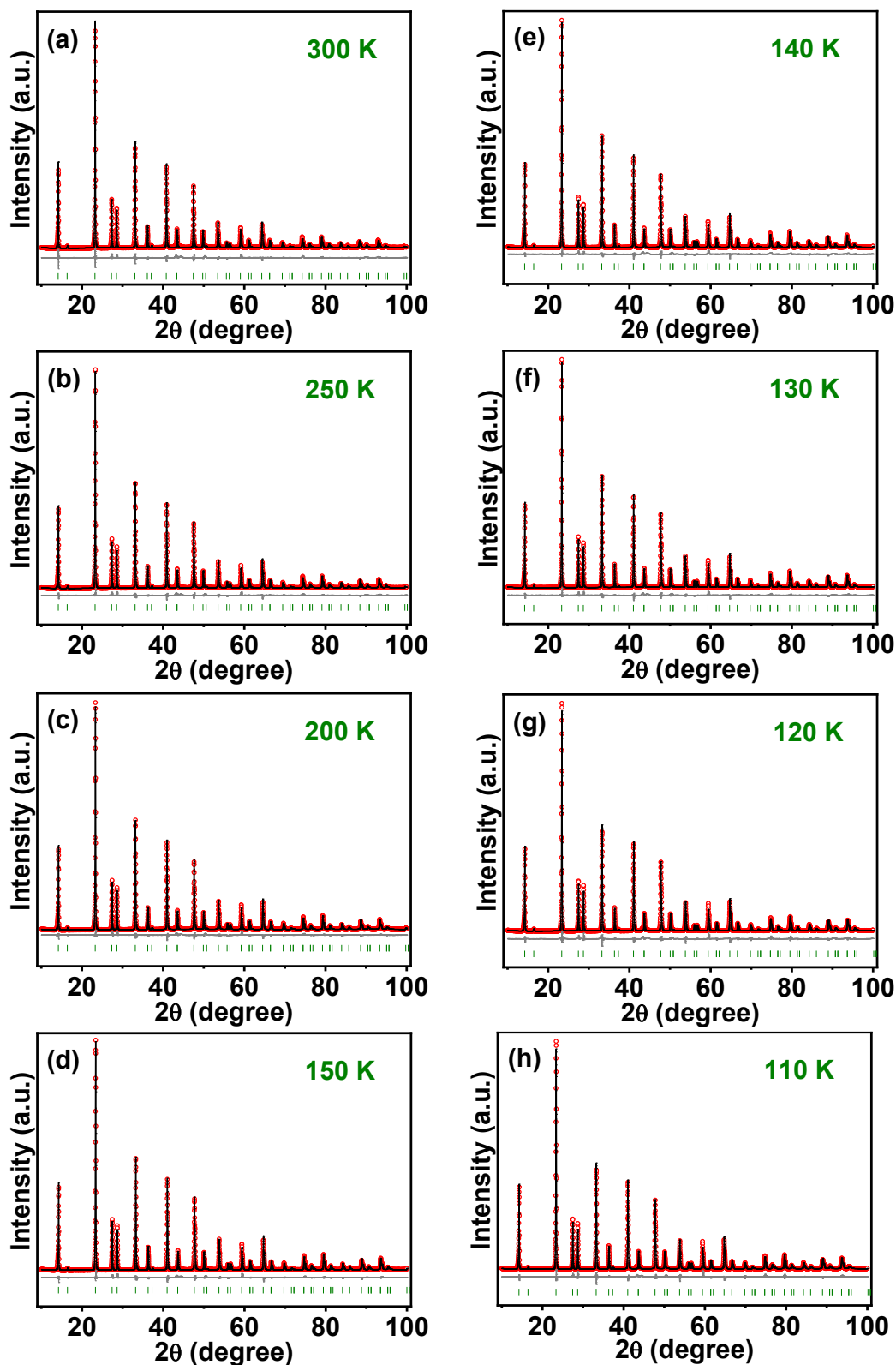


Figure 2A.11: Rietveld refinement of the powder XRD patterns of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ measured in the temperature range of 300-110 K. The main refinement parameters are shown Table 2A.3. In this temperature range, the sample exhibit cubic phase with space group $Fm\bar{3}m$.

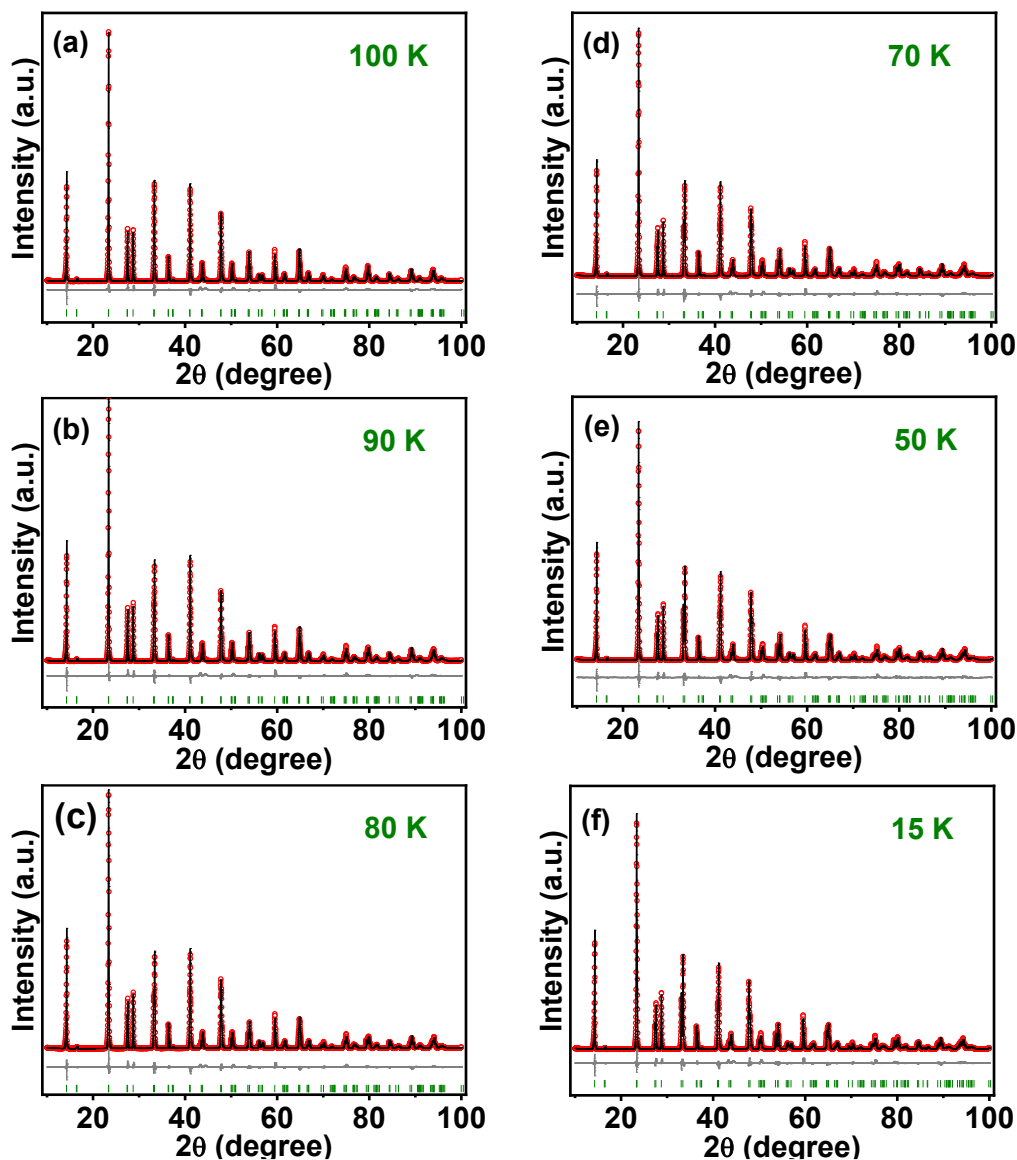


Figure 2A.12: Rietveld refinement of the powder XRD patterns of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ measured in the temperature range of 100-15 K. The main refinement parameters are shown Table 2A.3. In this temperature range, the sample exhibit tetragonal phase with space group $I4/mmm$.

Table 2A.3 represents the cell parameters obtained in cubic system from 300-11 K and tetragonal system from 100-15 K. At lower temperature “a” decreases from 300-15 K whereas “c” elongates below 110 K. The total unit cell volume contract with lowering the temperature starting from 300 to 15 K.

Table 2A.4 represents the corresponding Na-Cl and Bi-Cl bond lengths. In cubic structure all six bond length appear to be equal where in tetrahedral form, four equatorial bonds appear to be same and contracted than two axial bonds.

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Table 2A.3: Main parameters of processing and refinement of powder XRD patterns of 0.7% Mn²⁺-doped Cs₂NaBiCl₆ at different temperatures.

T (K)	Space Group	Cell parameters (Å), Cell Volume (Å ³)	R_{wp} , R_p , R_B , χ^2
300	<i>Fm-3m</i>	$a = 10.83284(15)$, $V = 1271.24(5)$	8.66, 6.01, 2.87, 2.06
250	<i>Fm-3m</i>	$a = 10.81866(15)$, $V = 1266.25(5)$	8.39, 5.47, 2.87, 1.99
200	<i>Fm-3m</i>	$a = 10.80168(15)$, $V = 1260.30(5)$	8.4, 5.47, 2.96, 2.0
150	<i>Fm-3m</i>	$a = 10.78538(13)$, $V = 1254.60(5)$	8.68, 5.56, 3.0, 2.07
140	<i>Fm-3m</i>	$a = 10.78202(13)$, $V = 1253.43(5)$	8.61, 5.4, 2.97, 2.05
130	<i>Fm-3m</i>	$a = 10.77893(12)$, $V = 1252.35(4)$	8.58, 5.47, 2.94, 2.04
120	<i>Fm-3m</i>	$a = 10.77555(14)$, $V = 1251.17(5)$	8.71, 5.62, 3.06, 2.07
110	<i>Fm-3m</i>	$a = 10.7711(2)$, $V = 1249.64(7)$	9.88, 6.82, 2.94, 2.35
100	<i>I4/mmm</i>	$a = 7.60318(11)$, $c = 10.7915(2)$, $V = 623.84(2)$	9.08, 6.08, 3.06, 2.16
90	<i>I4/mmm</i>	$a = 7.59727(11)$, $c = 10.79930(19)$, $V = 623.32(2)$	9.03, 6.07, 3.11, 2.15
80	<i>I4/mmm</i>	$a = 7.59181(11)$, $c = 10.80705(18)$, $V = 622.87(2)$	9.04, 6.22, 2.95, 2.15
70	<i>I4/mmm</i>	$a = 7.58735(11)$, $c = 10.81222(18)$, $V = 622.44(2)$	9.38, 6.52, 3.06, 2.23
50	<i>I4/mmm</i>	$a = 7.57960(11)$, $c = 10.82254(18)$, $V = 621.76(2)$	9.56, 6.74, 3.18, 2.28
15	<i>I4/mmm</i>	$a = 7.57492(11)$, $c = 10.82865(18)$, $V = 621.34(2)$	9.74, 6.84, 0.0, 2.32

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Table 2A.4: Main bond lengths (Å) of 0.7% Mn²⁺-doped Cs₂NaBiCl₆ at temperatures from 300-15 K.

T = 300 K			
Na—Cl	2.7710(32)	Na—Cl ⁱⁱⁱ	2.773(3)
Bi—Cl	2.6453(32)	Bi—Cl ^{iv}	2.645(3)
T = 250 K			
Na—Cl	2.7630(32)	Na—Cl ⁱⁱⁱ	2.763(3)
Bi—Cl	2.6462(32)	Bi—Cl ^{iv}	2.645(3)
T = 200 K			
Na—Cl	2.7565(32)	Na—Cl ⁱⁱⁱ	2.753(3)
Bi—Cl	2.6442(32)	Bi—Cl ^{iv}	2.645(3)
T = 150 K			
Na—Cl	2.7416(32)	Na—Cl ⁱⁱⁱ	2.743(3)
Bi—Cl	2.6510(32)	Bi—Cl ^{iv}	2.655(3)
T = 140 K			
Na—Cl	2.7472(32)	Na—Cl ⁱⁱⁱ	2.743(3)
Bi—Cl	2.6437(32)	Bi—Cl ^{iv}	2.645(3)
T = 130 K			
Na—Cl	2.7443(32)	Na—Cl ⁱⁱⁱ	2.743(3)
Bi—Cl	2.6451(32)	Bi—Cl ^{iv}	2.645(3)
T = 120 K			
Na—Cl	2.7423(32)	Na—Cl ⁱⁱⁱ	2.742(3)
Bi—Cl	2.6453(32)	Bi—Cl ^{iv}	2.645(3)
T = 110 K			
Na—Cl	2.7423(32)	Na—Cl ⁱⁱⁱ	2.742(3)
Bi—Cl	2.6453(32)	Bi—Cl ^{iv}	2.645(3)
T = 100 K			
Bi—Cl ⁱ	2.6279(30)	Bi—Cl ²	2.6719(86)
T = 90 K			
Na—Cl ⁱ	2.7451(30)	Na—Cl ²	2.7343(64)
Bi—Cl ⁱ	2.6269(30)	Bi—Cl ²	2.6652(64)
T = 80 K			
Na—Cl ⁱ	2.7483(30)	Na—Cl ²	2.7237(86)
Na—Cl ⁱ	2.7399(30)	Na—Cl ²	2.7352(54)
Bi—Cl ⁱ	2.6282(30)	Bi—Cl ²	2.6682(54)
T = 70 K			
Na—Cl ⁱ	2.7361(30)	Na—Cl ²	2.7398(54)
Bi—Cl ⁱ	2.6288(30)	Bi—Cl ²	2.6662(54)
T = 50 K			
Na—Cl ⁱ	2.7323(30)	Na—Cl ²	2.7467(43)
Bi—Cl ⁱ	2.6272(30)	Bi—Cl ²	2.6645(43)
T = 15 K			
Na—Cl ⁱ	2.7263(30)	Na—Cl ²	2.7461(43)
Bi—Cl ⁱ	2.6299(30)	Bi—Cl ²	2.6681(43)

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Table 2A.5: Fractional atomic coordinates and isotropic displacement parameters ($\text{\AA}^2$) of 0.7% Mn²⁺-doped Cs₂NaBiCl₆ in the cubic structure in the temperature range 300-110 K.

Atom	x	y	z	B _{iso}	Occ.
T = 300 K					
Na	0	0	0	1.52(19)	1
Bi	0.5	0	0	1.36(7)	1
Cs	0.25	0.25	0.25	3.35(8)	1
Cl	0.2558(3)	0	0	3.22(9)	1
T = 250 K					
Na	0	0	0	1.29(18)	1
Bi	0.5	0	0	1.11(6)	1
Cs	0.25	0.25	0.25	2.78(7)	1
Cl	0.2554(3)	0	0	2.78(8)	1
T = 200 K					
Na	0	0	0	0.73(17)	1
Bi	0.5	0	0	0.92(6)	1
Cs	0.25	0.25	0.25	2.27(6)	1
Cl	0.2552(3)	0	0	2.35(8)	1
T = 150 K					
Na	0	0	0	0.66(17)	1
Bi	0.5	0	0	0.58(6)	1
Cs	0.25	0.25	0.25	1.55(6)	1
Cl	0.2542(3)	0	0	1.85(7)	1
T = 140 K					
Na	0	0	0	0.51(17)	1
Bi	0.5	0	0	0.58(6)	1
Cs	0.25	0.25	0.25	1.55(6)	1
Cl	0.2548(3)	0	0	1.82(7)	1
T = 130 K					
Na	0	0	0	0.53(16)	1
Bi	0.5	0	0	0.54(6)	1
Cs	0.25	0.25	0.25	1.47(6)	1
Cl	0.2546(3)	0	0	1.73(7)	1
T = 120 K					
Na	0	0	0	0.50(17)	1
Bi	0.5	0	0	0.53(6)	1
Cs	0.25	0.25	0.25	1.38(6)	1
Cl	0.2545(3)	0	0	1.70(7)	1
T = 110 K					
Na	0	0	0	0.9(2)	1
Bi	0.5	0	0	0.53(6)	1
Cs	0.25	0.25	0.25	1.34(6)	1
Cl	0.2546(3)	0	0	1.80(8)	1

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Table 2A.6: Fractional atomic coordinates and isotropic displacement parameters ($\text{\AA}^2$) of 0.7% Mn²⁺-doped Cs₂NaBiCl₆ MCs in tetragonal structure in the temperature range 100-15 K.

Atom	x	y	z	B _{iso}	Occ.
T = 100 K					
Na	0	0	0	0.96(19)	1
Bi	0	0	0.5	0.46(6)	1
Cs	0	0.5	0.25	1.25(6)	1
Cl1	0.7444(4)	0.7444(4)	0	1.80(16)	1
Cl2	0	0	0.2524(8)	1.9(3)	1
T = 90 K					
Na	0	0	0	1.2(2)	1
Bi	0	0	0.5	0.43(6)	1
Cs	0	0.5	0.25	1.18(6)	1
Cl1	0.7445(4)	0.7445(4)	0	2.00(14)	1
Cl2	0	0	0.2532(6)	1.8(2)	1
T = 80 K					
Na	0	0	0	1.4(2)	1
Bi	0	0	0.5	0.31(6)	1
Cs	0	0.5	0.25	1.05(6)	1
Cl1	0.7448(4)	0.7448(4)	0	2.05(12)	1
Cl2	0	0	0.2531(5)	1.56(19)	1
T = 70 K					
Na	0	0	0	1.5(2)	1
Bi	0	0	0.5	0.25(6)	1
Cs	0	0.5	0.25	0.95(6)	1
Cl1	0.7450(4)	0.7450(4)	0	1.97(12)	1
Cl2	0	0	0.2534(5)	1.64(19)	1
T = 50 K					
Na	0	0	0	1.8(2)	1
Bi	0	0	0.5	0.23(6)	1
Cs	0	0.5	0.25	0.86(6)	1
Cl1	0.7451(4)	0.7451(4)	0	2.19(11)	1
Cl2	0	0	0.2538(4)	1.52(16)	1
T = 15 K					
Na	0	0	0	2.1(3)	1
Bi	0	0	0.5	0.20(6)	1
Cs	0	0.5	0.25	0.66(6)	1
Cl1	0.7455(4)	0.7455(4)	0	2.30(11)	1
Cl2	0	0	0.2536(4)	1.34(15)	1

In cubic system atomic coordinates of Na, Bi and Cs have atomic coordinates 0, 0.5 and 0.25. In tetragonal form their coordinates change to 0, 0, 0 respectively indicating octahedral rotation. For all six Cl, coordinate changes due to lattice

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contraction only from 300-110 K. Then four equatorial Cl1 have different atomic coordinates than Cl2 axial ones in the tetragonal structure from 100-15K.

The pseudo color map in Figure 2A.13a and b, highlights the cubic to tetragonal phase transition of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ below 110 K, by presenting XRD peak splitting at 2θ around 33.3° . In the cubic phase, all three (400), (004), and (040) planes diffract at the same 2θ value, yielding one peak of higher intensity, which splits into two peaks in the tetragonal phase with expected intensity ratio, as reflected through the colour scale bar. The undoped $\text{Cs}_2\text{NaBiCl}_6$ also shows a very similar phase transition, as reflected by the pseudo colour map in Figure 2A.13a-c. For both samples, the phase transition temperature is between 110 and 100 K. Our data show that the Mn^{2+} -doping in $\text{Cs}_2\text{NaBiCl}_6$ does not change the phase transition behavior. There are instances in literature where lattice doping of perovskites can significantly change the transition temperature from the tetragonal to cubic phase, but this occurs at a higher (4–7%) doping concentration.^{46, 47} In Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$, the dopant concentration relevant for Mn^{2+} PL is small (0.1–1.3%, see Figure 2A.7b), and the doping does not significantly alter the phase transition behavior.

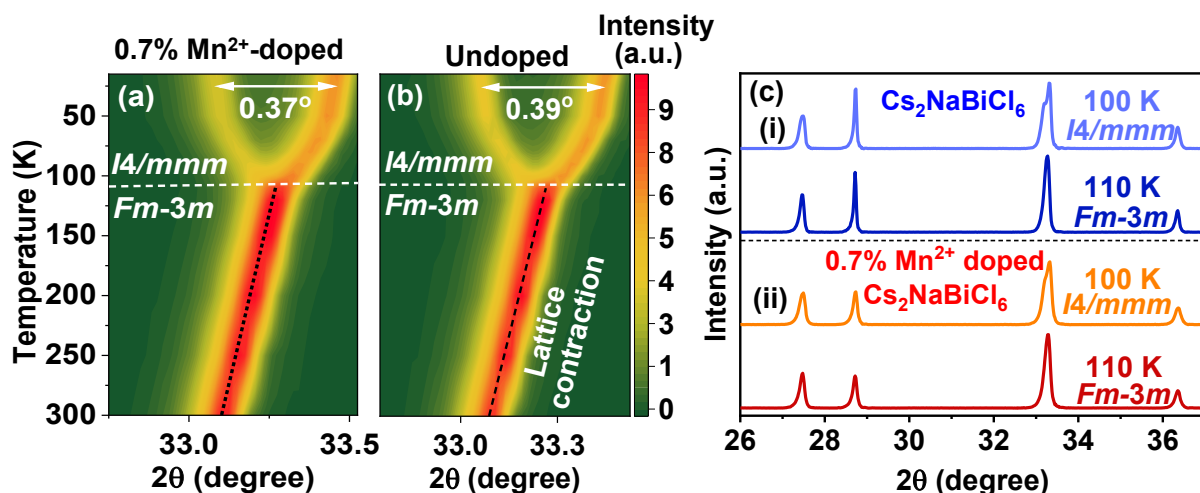


Figure 2A.13: Pseudo color map of the temperature-dependent powder XRD patterns showing the effect of phase transition on the (400) peaks of (c) 0.7% Mn^{2+} -doped and (d) undoped $\text{Cs}_2\text{NaBiCl}_6$ (c) Powder XRD patterns of (i) undoped $\text{Cs}_2\text{NaBiCl}_6$ and (ii) 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ at temperatures just above (110 K) and below (100 K) the phase transition.

Figure 2A.14a shows the variation of the unit cell parameters of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ with temperature. In the temperature range of 300–110 K, the cubic

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phase cell parameter “ a ” ($a = b = c$) decreases with decreasing temperature. In the temperature range of 110 to 15 K, the tetragonal cell parameter “ a ” ($a = b$) decreases with decreasing temperature, but “ c ” increases with decreasing temperature. These results show that below the tetragonal phase transition temperature, the elongation of the c -axis of the unit cell continues to increase with decreasing temperature. The unit cell volume can be estimated for both crystal phases, and the data for 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ are shown in Figure 2A.14b. A systematic decrease in the unit cell volume is observed throughout temperature range of 300 to 15 K encompassing both cubic and tetragonal phases.

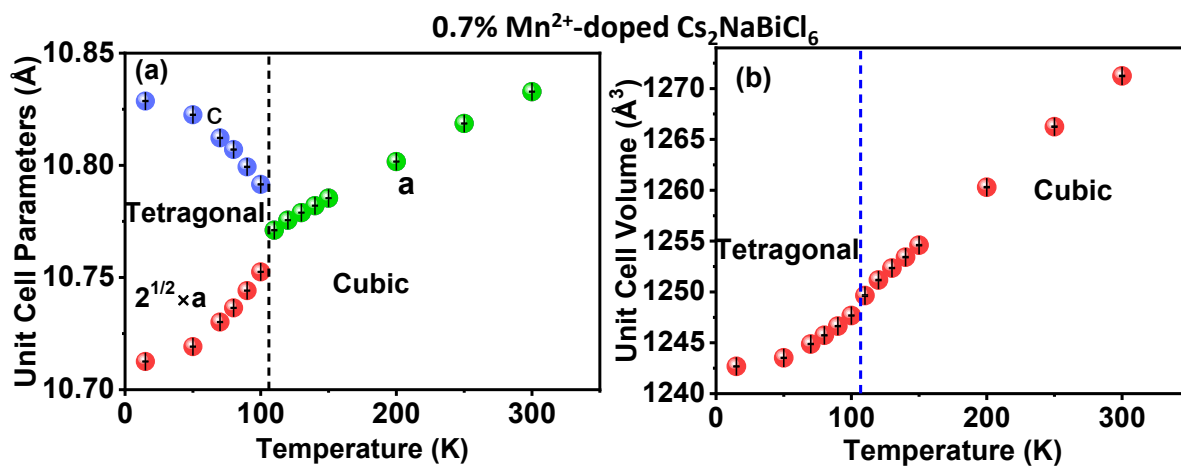


Figure 2A.14: (a) Cell parameters and (b) volume of unit cell of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ measured at different temperatures.

2A.3.4: Temperature-Dependent PL and Local Structure around Mn^{2+} Dopant Ion

Powder XRD data (Figure 2A.9-2A.14) confirms the phase transition below 110 K, with elongation of the c -axis with decreasing temperature. Does this structural change influence the PL of Mn^{2+} d -electron emission, which depends upon the local structure around Mn^{2+} dopant ion? Figure 2A.15a shows the PL emission spectra of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ at selective temperatures. The pseudo color map in Figure 2A.15b shows more temperature-dependent PL spectra together. At lower temperatures, the PL excitation (PLE) maxima shifts a bit, as shown in Figure 2A.15c. Consequently, for PL emission measurements at different temperatures (Figure 2A.15a and b), and we have excited the sample with slightly different excitation wavelengths, based on their PLE maxima. The change in PL peak position and full width at half-maximum are shown in Figure 2A.15d. Clearly, the PL peak position shifts

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to lower energy (longer wavelength) with decreasing temperature. Similar PL shift has been observed in the case of Mn^{2+} -doped $\text{Cs}_2\text{Na}_{1-x}\text{Ag}_x\text{BiCl}_6$ and Mn^{2+} -doped $\text{Cs}_2\text{NaInCl}_6$ double perovskites.^{36, 37} This shift can be explained by the Tanabe–Sugano diagram (T-S diagram) for the d^5 system, as shown in Figure 2A.16. The 4T_1 to 6A_1 PL transition energy depends on the crystal field strength. The lattice contracts with decreasing the temperature; consequently the crystal field strength increases with decreases in temperature, which in turn decreases the 4T_1 to 6A_1 transition energy.^{31, 36, 47} But the change in peak position is monotonous with temperature, without observing any sudden change near the phase transition temperature (100–110 K).

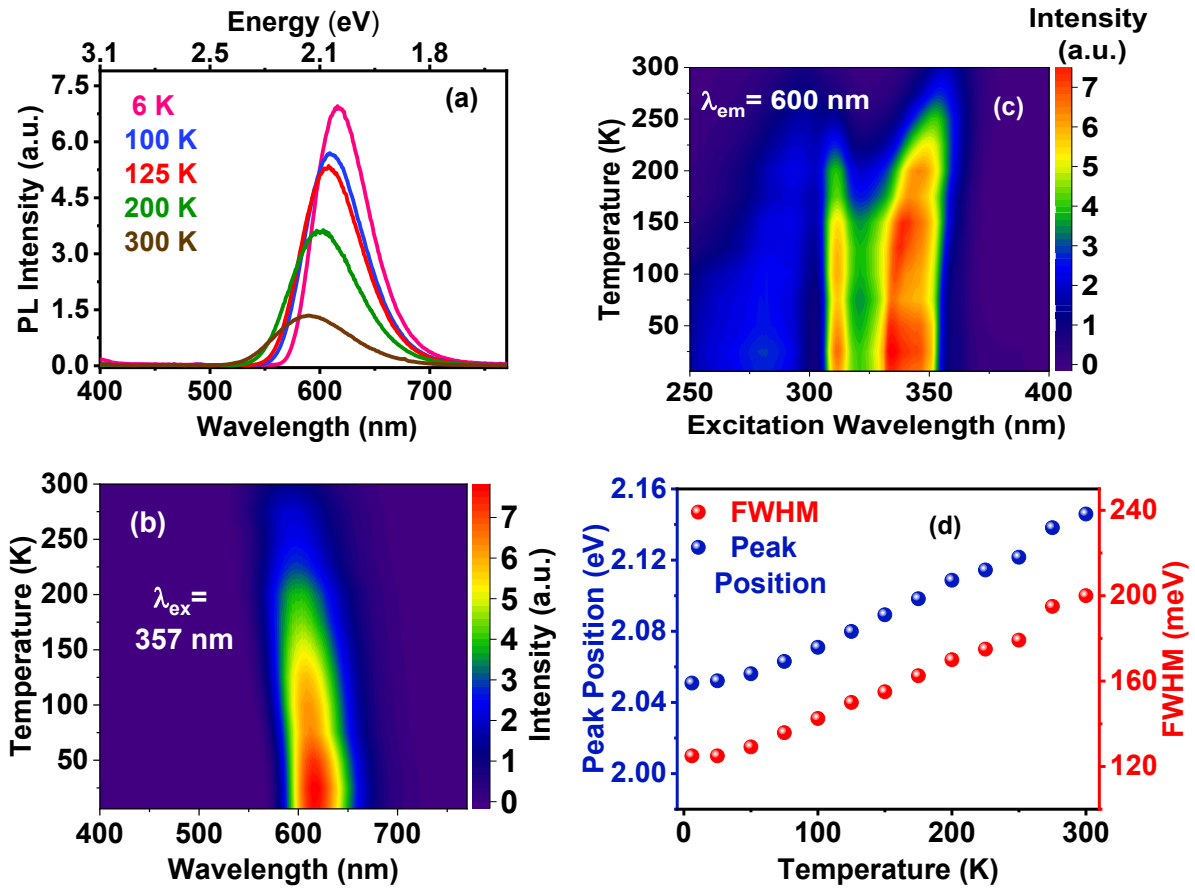


Figure 2A.15: (a) Temperature-dependent PL spectra of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$. The excitation wavelength was slightly varied with the temperature. For 300, 200, 125, 100, and 6 K, the excitation wavelengths are 359, 346, 338, 336, and 334 nm, respectively. (b) Pseudo color map of the temperature-dependent PL spectra including data at many more temperatures, compared to panel (a). (c) Pseudo color map of the temperature-dependent PL excitation (PLE) spectra of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$. (d) Variation of PL peak position and FWHM of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ with measurement temperature.

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Likewise, FWHM decreases with temperature because of the decrease in electron–phonon coupling at lower temperatures, but here again, no signature of phase transition is observed in the temperature range of 100–110 K. Figure 2A.17 estimates the value of Huang–Rhys parameter (S) as 7.1, reflecting a moderate electron–phonon coupling that is observed for Mn^{2+} d -electron emission.⁴⁸

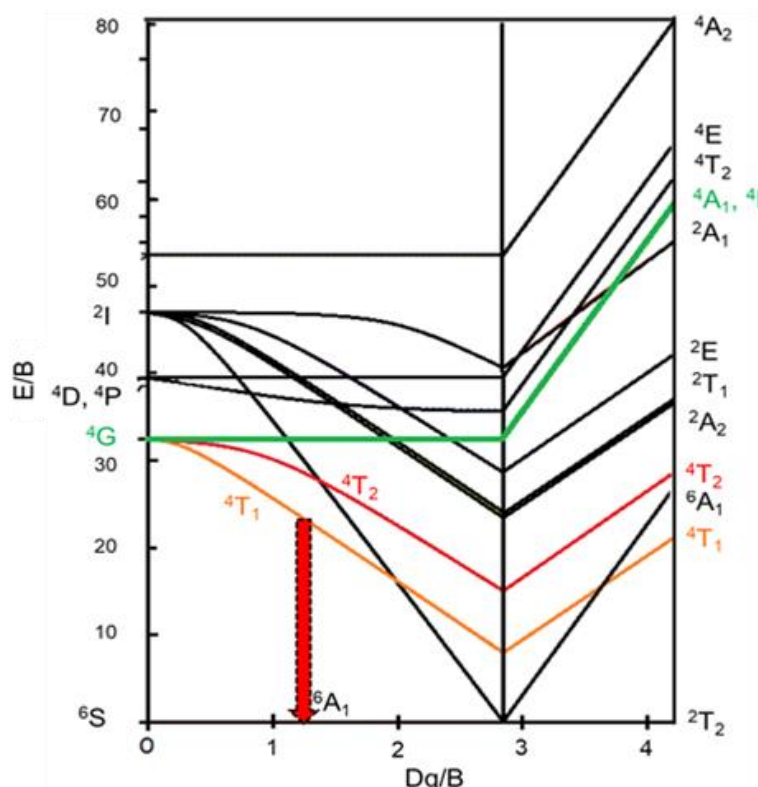


Figure 2A.16: T-S diagram of d^5 electronic configuration in octahedral crystal environment.⁴⁵ Mn^{2+} ion (MnCl_6^{4-}), in Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ represent a high-spin, weak field d^5 electronic configuration. The 4T_1 to 6A_1 transition indicated by the red arrow is responsible for the Mn^{2+} PL.

The variation of PL intensity with temperature is shown in Figure 2A.18. The emission intensity increases with decreasing temperature starting from 300 to 25 K because of the suppression of nonradiative emission at lower temperature. Then from 25 to 7 K the intensity decreases a bit, but the reason is unexplained. But the trend in integrated PL intensity does not deviate near phase-transition temperature. The variation of emission intensity also does not show any influence of the structural phase transition. We also note that all of the temperature-dependent changes in structure and PL properties are reversible in nature.

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The dimensionless Huang–Rhys parameter (S), which is a measure of electron–phonon coupling, can be estimated from the temperature (T)-dependent variation of full-width-at-half-maxima ($FWHM$) of PL spectra, following eq (4), where $\hbar$ is the Planck constant, ω_{ph} is phonon frequency, and k_B is Boltzmann constant. Figure 2A.17 gives the values of $FWHM$ of Mn²⁺ emission and the electron-phonon coupling value of 7.1 and phonon energy of 26 meV.

$$FWHM = 2.36\sqrt{S}\hbar\omega_{ph}\sqrt{\coth\left(\frac{\hbar\omega_{ph}}{2k_B T}\right)} \quad (4)$$

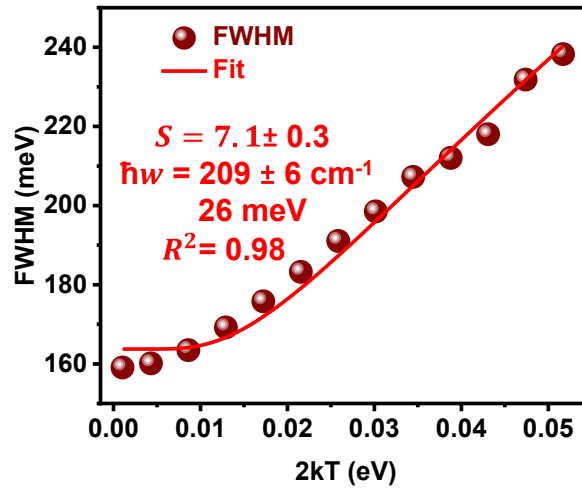


Figure 2A.17: Fitting of temperature-dependent variation of FWHM of Mn²⁺ emission from 0.7% Mn²⁺ -doped Cs₂NaBiCl₆ using the Huang-Rhys equation shown equation-4.

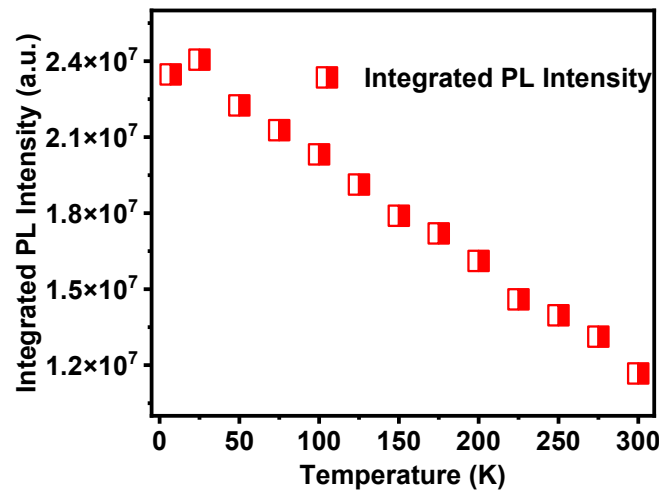


Figure 2A.18: Change in integrated PL intensity of 0.7% Mn²⁺ -doped Cs₂NaBiCl₆ with measurement temperature.

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We have also measured PL decay profiles of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ at different temperatures, as shown in Figure 2A.19 in cubic phase in and 2A.20 in tetragonal phase. The decay profiles are fitted using equation- 2, and the best-fit parameters are shown in Table 2A.7. The Mn^{2+} emission lifetime increases with decreasing temperature because of the suppression of nonradiative channels. But the increase in lifetime is also systematic, without showing any sudden change around the phase-transition temperature. All features of the steady-state PL and PL decay data do not show any influence of the phase transition.

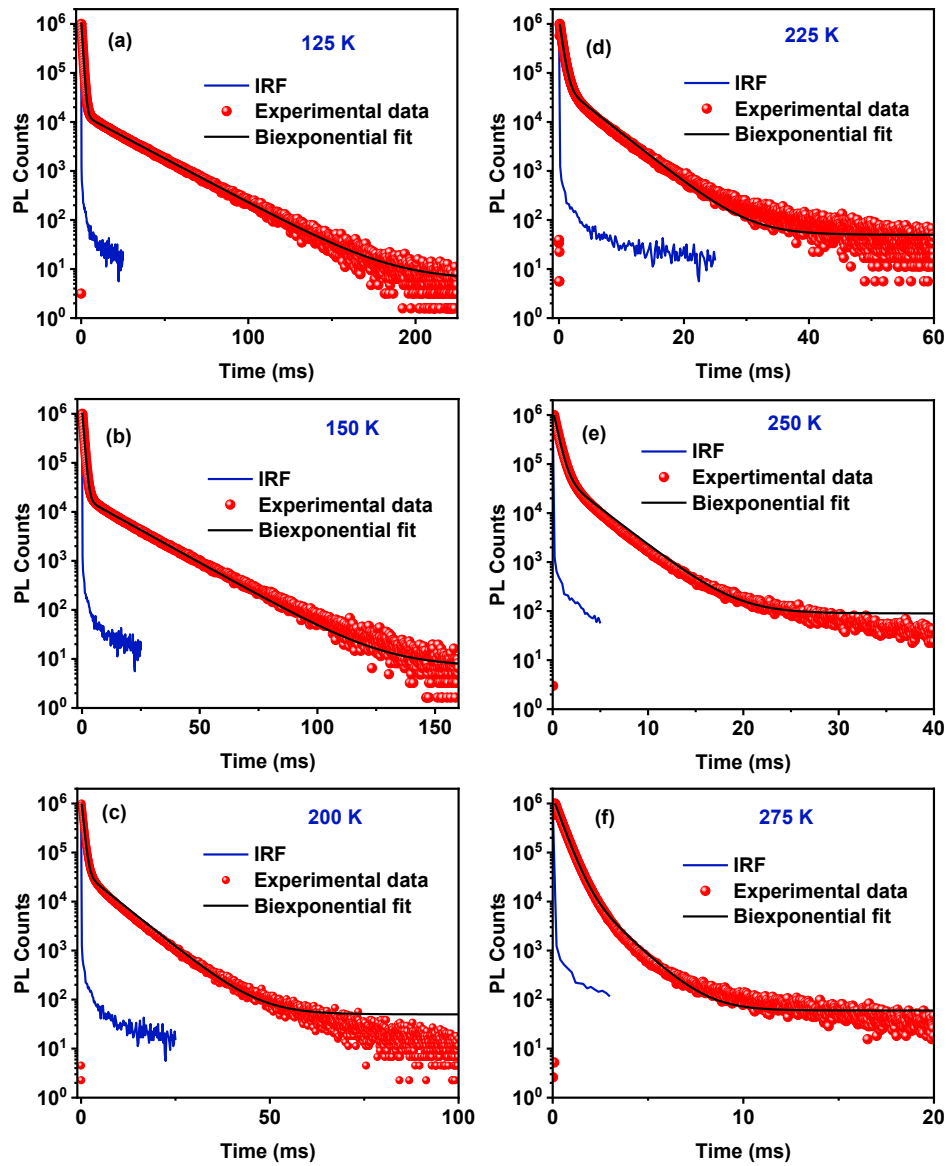


Figure 2A.19: PL decay profiles of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ at different measurement temperature from 125 to 275 K in cubic phase. The experimental profiles are fitted using a bi-exponential decay (equation 2 of the manuscript). The best-fit parameters are shown in Table 2A.7.

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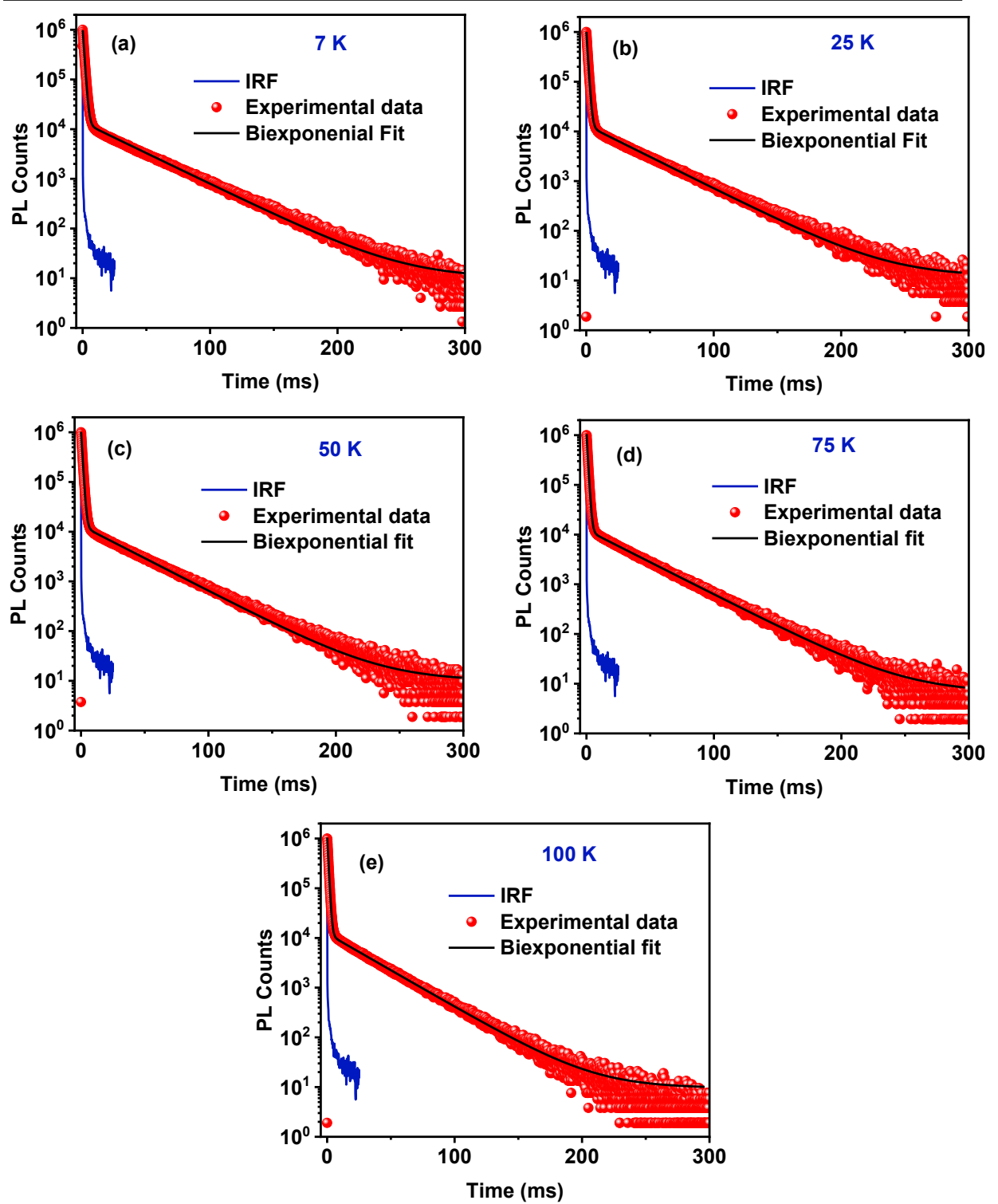


Figure 2A.20: PL decay profiles of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ at different measurement temperature from 7 to 100 K in tetragonal phase. The experimental profiles are fitted using a bi-exponential decay (equation 2). The best-fit parameters are shown in Table 2A.7. The blue curve represents the instrument response function.

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Table 2A.7: The best-fit parameters obtained by bi-exponential fitting of PL decay profiles shown in Figure S9-10. As defined in equation-2, τ_n is PL lifetime with contribution A_n , where $n = 1, 2$. τ_{avg} calculated using equation 3.

Temperature	A ₁ %	τ_1 (ms)	A ₂ %	τ_2 (ms)	τ_{avg} (ms)
7 K	99	1.1	1	35.0	9.3
25 K	99	1.1	1	34.0	8.9
75 K	99	1.0	1	33.5	9.2
100 K	99	0.9	1	29.4	7.9
125 K	99	0.8	1	24.0	6.2
150 K	98	0.7	2	17.0	6.1
200 K	97	0.6	3	7.0	2.3
225 K	96	0.5	4	4.3	1.5
250 K	95	0.5	5	2.9	1.1
275 K	96	0.4	4	1.2	0.5
300 K	67	0.2	33	0.5	0.4

The cubic to tetragonal phase transition changes the octahedral coordination around the Bi³⁺ (and Na⁺), but the PL data does not suggest any major change in octahedral coordination around Mn²⁺ dopants. The powder XRD data provides an averaged out picture and is insufficient to probe the local structure around the Mn²⁺ dopant ions. To probe the local structure around the Mn²⁺ ion, we employ temperature-dependent EPR spectroscopy, as shown in Figure 2A.21. The hyperfine splitting energy remains at 9 mT with $g = 1.98$ both at 300 and 85 K, before and after the phase transition. This similarity suggests the local octahedral coordination around the Mn²⁺ dopant ion does not change much because of the phase transition, and is also

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supported by the observation that the nature of Mn^{2+} emission does not change by the phase transition.

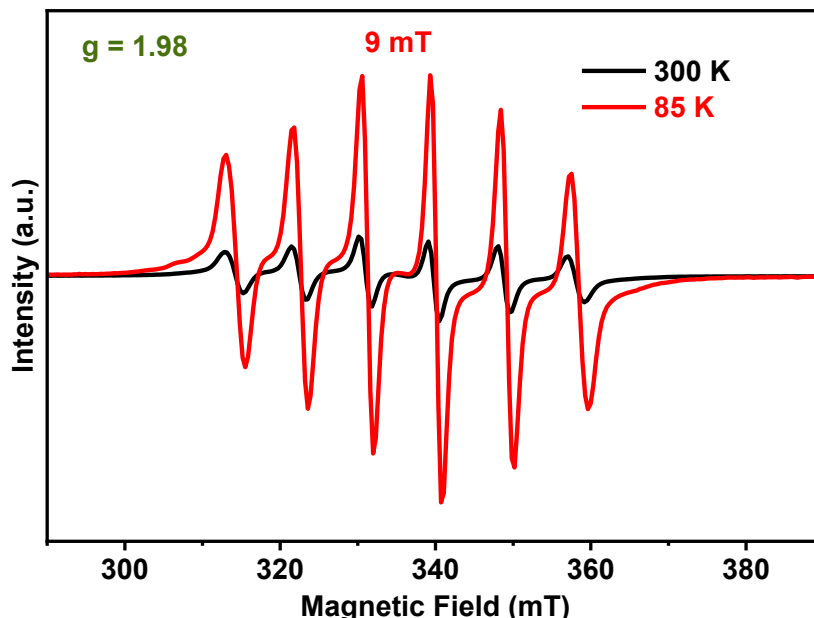


Figure 2A.21: X-band EPR spectra of 0.7% Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ at 300 and 85 K.

2A.4 Conclusions

We have prepared Mn^{2+} -doped $\text{Cs}_2\text{NaBiCl}_6$ double perovskites using a hydrothermal method with varying dopant concentrations between 0 to 1.3%. The doping introduces an orange-red PL because of $^4\text{T}_1$ to $^6\text{A}_1$ Mn^{2+} $d-d$ transition, with a maximum intensity for 0.7% doping. Both the undoped and 0.7% Mn^{2+} -doped samples show very similar temperature-dependent structural phase transition. Both samples exhibit a cubic phase with $Fm-3m$ space group between 300 and 110 K, transitioning to tetragonal ($I4/mmm$) phase with elongated c -axis below 110 K. The extent of c -axis elongation increases systematically with decreasing temperature until 15 K, while retaining the tetragonal phase. The c -axis elongation distorts the $[\text{BiCl}_6]^{3-}$ octahedron, but does not affect the PL and EPR signature of Mn^{2+} dopants, which are expected to substitute the Bi^{3+} sites. PL peak shifts to lower energy due to lattice contraction, while changes in PL FWHM, intensity and lifetimes result from reduced electron-phonon coupling and nonradiative decay channels with decreasing temperature from 300 to 6 K. However, no signature of the structural phase transitions is observed in the Mn^{2+} PL. Also, the EPR spectra at 300 K (cubic phase) and 85 K (tetragonal phase) show identical hyperfine splitting of 9 mT with $g = 1.98$. These findings suggest that Mn^{2+}

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local structure remains largely unaffected by the host lattice's global phase transition, providing stability to the Mn²⁺ PL. This insight could extend to other doped halide double perovskites, advancing them for various optoelectronic applications.

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Chapter 2B

***Temperature-Dependent Phase Transition and Near-infrared
Emission of Mo^{3+} -Doped $\text{Cs}_2\text{NaBiCl}_6$ Double Perovskite***

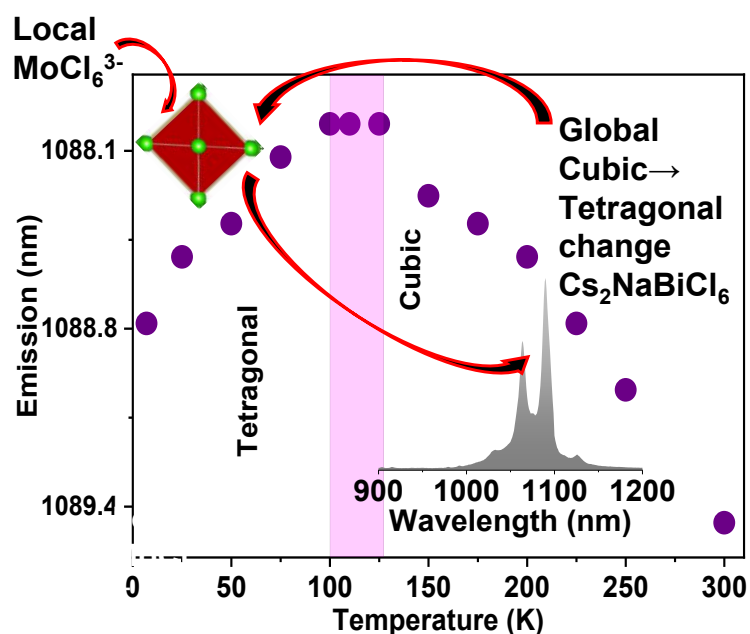
Chapter 2B

Temperature-Dependent Phase Transition and Near-infrared Emission of Mo³⁺-Doped Cs₂NaBiCl₆ Double Perovskite

Abstract

Cubic to tetragonal structural change in Cs₂NaBiCl₆ below 110 K, has been probed by narrow near-infrared emission of Mo³⁺, when doped into its lattice. The near-infrared emission originates from the intra-configurational spin-flip *d-d* transition of Mo³⁺, showing a narrow full width half maxima (FWHM) around 10 meV, at room temperature. The narrow FWHM becomes a sensitive probe to monitor minor temperature-dependent change in the emission energy, owing to the structural phase transition around 100 K. In addition, temperature-dependent powder X-ray diffraction patterns corroborate the phase transition of Mo³⁺-doped Cs₂NaBiCl₆. The phase transition is expected to distort the local environment around the Mo³⁺, particularly distorting the [MoCl]₆³⁻ octahedra, which in turn influence the NIR mission.

Graphical Abstract



Chapter 2B

Temperature-Dependent Phase Transition and Near-infrared Emission of Mo^{3+} -Doped $\text{Cs}_2\text{NaBiCl}_6$ Double Perovskite

2B.1 Introduction

Among the transition metals, Mn^{2+} , Cr^{3+} , Mo^{3+} , Mn^{5+} , Ni^{2+} are the most explored ones showing $d-d$ transitions (emission). But in octahedral sites like in perovskites, some selective Mn^{2+} ,¹ Cr^{3+} ,² Mo^{3+} ,³ elements emit when doped. Among these three, Mn^{2+} is well explored for orange to red emission, may it be doped in lead based halide perovskite (APbX_3)⁴⁻⁶ or lead-free double perovskites ($\text{A}_2\text{BB}'\text{X}_6$)⁷⁻⁹ irrespective size or dimensions from bulk¹⁰ or nanocrystals.⁵ While, in tetrahedral coordination Mn^{2+} shows green emission.^{11, 12} But in halide perovskites since the dopants form six coordinated octahedra with halides, the orange to red emission is considered for further discussion. This emission retains also in zero,^{13, 14} one,^{15, 16} two¹⁷⁻²¹ or three dimensionally connected halide based perovskite derivatives. But from host to host the emission energy, lifetime, FWHM changes, not significantly but in a noticeable extent. This is because unlike the lanthanides, where $f-f$ transitions are atomic like and does not get perturbed by the surroundings, d orbitals being diffused can be sensitive towards the surrounding ligands, geometry (perfect octahedral, tetragonally distorted octahedra etc.) lattice vibrations.²²

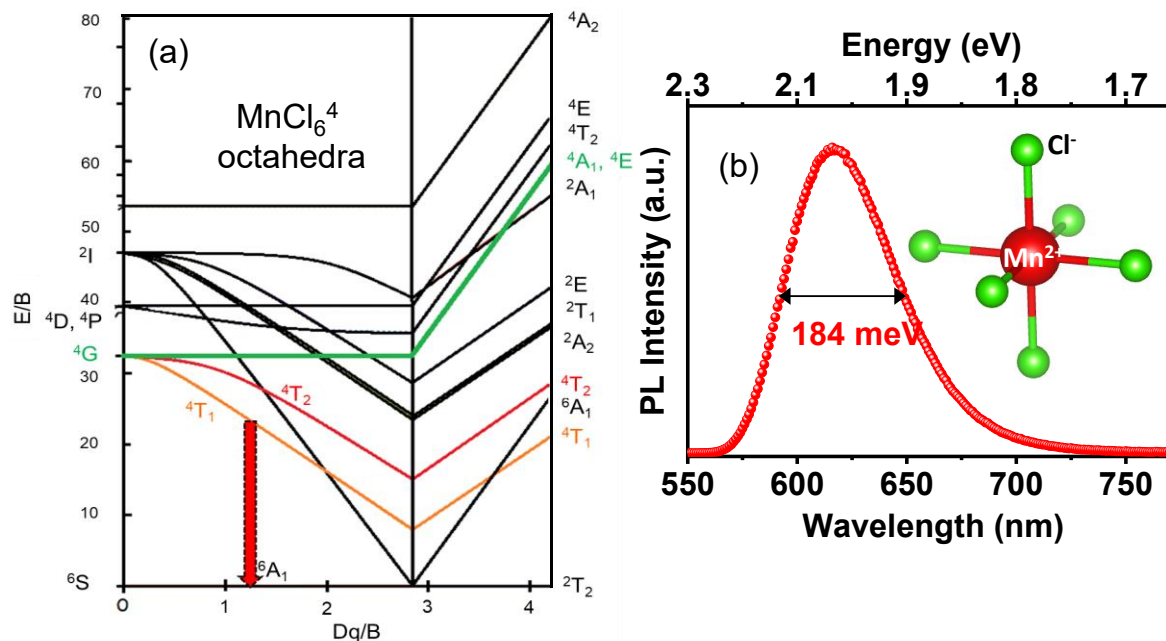


Figure 2B.1.(a) Tanabe-Sugano (T-S) diagram of Mn^{2+} (d^5) in octahedral coordination showing the emission involving first excited state and ground state (red arrow). (b) PL emission of Mn^{2+} doped $\text{Cs}_2\text{NaBiCl}_6$ microcrystals at room temperature (excitation wavelength = 346 nm).

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This orange to red emission is the result of the $d-d$ transition from first excited state (${}^4\text{T}_1$) to ground state (${}^6\text{A}_1$) (Figure 2B.1a). This emission has very broad feature, for example, FWHM ~ 180 meV when doped in $\text{Cs}_2\text{NaBiCl}_6$ at room temperature as shown in Figure 2B.1b. The huge FWHM is mainly due to lattice vibrations that leads to broadening (known as emission-electron-phonon coupling).²³ This emission is so dominated by electron-phonon coupling that the minute change in emission behavior due to crystal structure change from cubic to tetragonal, may be suppressed. Thereby, we choose an emissive transition metal which shows a narrower emission so that the lattice vibration effect on the emission is low or negligible than phase transition effect changing the local structure around the metal center.

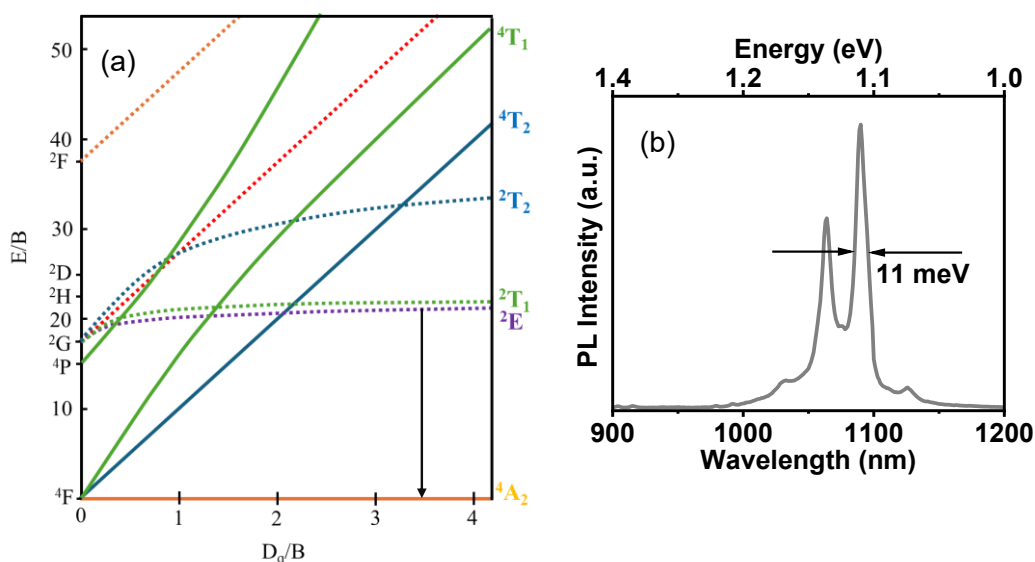


Figure 2B.2. (a) (T-S) diagram for d^3 system in octahedral coordination showing the emission from ${}^2\text{E}$ to ${}^4\text{A}_2$ state (black arrow). (b) Sharp emission from MoCl_6^{3-} octahedra in Mo^{3+} doped $\text{Cs}_2\text{NaBiCl}_6$ low FWHM.

Mo^{3+} is a d^3 system with 3 unpaired electrons. In presence of six Cl^- ligands the three electrons remain in lower energy t_{2g} . the value of Dq/B of Mo^{3+} , is found to be at stronger crystal field range, in case of $\text{Cs}_2\text{NaInCl}_6$. At this crystal field strength, the ground state is ${}^4\text{A}_2$, and the excited state is ${}^2\text{E}$, see the T-S diagram (dotted violet line in Figure 2B.2a). A sharp emission from ${}^2\text{E}$ to ${}^4\text{A}_2$ comes as shows by the black arrow. The ground state, ${}^4\text{A}_2$, consists of three electrons with same spin at three degenerate t_{2g} orbitals. In the first excited state ${}^2\text{E}$, one of the three electrons changes its spin and remains in same t_{2g} orbitals, thereby it is called intra-configurational spin flip

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Temperature-Dependent Phase Transition and Near-infrared Emission of Mo³⁺-Doped Cs₂NaBiCl₆ Double Perovskite

transition.^{24, 25} So, the transition is only due to one spin-flip of one electron in same t_{2g} orbital and least affected by the lattice vibrations. The flat parallel nature of 2E state with ground state, signifies the independence of the electronic states' energy much on surrounding lattice vibrations and emission is found to be sharp. At room temperature Mo³⁺ shows emission with FWHM of 8 meV when doped in Cs₂NaInCl₆.²⁶ But since this system does not show a phase transition at lower temperature, the effect of phase transition on this sharp emission could not be observed. So Mo³⁺ was doped in Cs₂NaBiCl₆, to understand how the sharp emission with FWHM 11 meV (Figure 2B.2b) behaves with the crystal structure change. The ground state geometry of the octahedra if changes, also expected to change the excited state dynamics of the same emission.

2B.2 Experimental Section

2A.2.1 Chemicals

Cesium chloride (CsCl, 99.9%, Sigma Aldrich), sodium chloride (NaCl, 99.999%, Sigma Aldrich), bismuth chloride (BiCl₃, 99.99%, Sigma Aldrich), molybdenum chloride (MoCl₃, 99.5%, Thermo Fisher Scientific) and hydrochloric acid (HCl, aqueous 37% w/w Sigma Aldrich), H₃PO₂ (50%, w/w, Avra). Ethanol (≥99.80%) is purchased from Rankem. All of the chemicals are used without any further purification.

2B.2.2 Synthesis of Mo³⁺ Doped Cs₂NaBiCl₆

Synthesis of Mo³⁺ doped Cs₂NaBiCl₆ is similar to Mn²⁺ doped Cs₂NaBiCl₆, the only difference is MoCl₃ has been used instead of MnCl₂, in stoichiometry of 2%, 0.3% and 0.05% with respect to Bi³⁺. H₃PO₂ has been added to maintain the reducing environment for Mo³⁺ following the reaction procedure for Mo³⁺ doped Cs₂NaInCl₆.²⁶

2B.2.3 Characterization

Characterization of undoped and Mo³⁺ doped Cs₂NaBiCl₆ were done following the same methods for Mn²⁺ doped Cs₂NaBiCl₆, discussed earlier in chapter 2A. Characterization includes temperature dependent PXRD, absorption, temperature, PL

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dependent photoluminescence excitation and lifetime measurement. Only for low temperature PL measurement the step size was changed to 0.25 nm.

2B.3 Results and Discussion

2B.3.1 Mo³⁺-doping: Structure and Optical Property at Room Temperature

The Mo³⁺ doping in Cs₂NaBiCl₆ host lattice may replace either Na⁺ or Bi³⁺ because of similar charge and size. Mo³⁺ has smaller Shannon ionic radii (69 pm) in six coordination than that of Na⁺ (102 pm) and Bi³⁺ (103 pm).²⁷ So, doping of Mo³⁺ in a small quantity will not change the overall crystal structure from its original (cubic) but may lead to change in d spacing due to shrinking the unit cell parameters of the lattice. As shown in Figure 2B.3a the PXRD pattern corresponding to undoped and 0.05-2% of Mo³⁺ doped samples are similar when compared with standard one (bottom most gray pattern), without presence of any additional peak, indicating the formation of phase pure samples upon doping. The only difference appears as, the peaks shift towards higher 2θ with increasing Mo³⁺ percentage. This is because Mo³⁺ incorporation leads to shrinkage to lattice d spacing, which leads to shift of peak position towards higher value, according to Bragg's law.²⁸

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

where, n = order of reflection, λ is wavelength of X-ray (Cu Kα = 1.5406 Å), d is spacing between planes, θ is the diffraction angle.

After confirming the phase purity of the prepared samples, Mo³⁺-doped Cs₂NaBiCl₆ is showing an intense NIR emission at 1063 and 1090 nm, shown in Figure 2B.3b similar to Mo³⁺-doped Cs₂NaInCl₆, reported recently by Nag and coworker.²⁶ The intensity of the NIR emission increases with increasing the doping percentage of Mo³⁺ and further increasing the Mo³⁺ doping percentage leads to formation of Cs₂NaMoCl₆ (100 % Mo³⁺ doping) as a impurity phase. As a result, the phase pure 2% Mo³⁺ doped Cs₂NaBiCl₆ was consider probing temperature dependent phase transition. The undoped host Cs₂NaBiCl₆ lattice is a wide band gap material, shows intense absorption at 316 and 340 nm (Figure 2B.3c) corresponding to Bi³⁺ ion's Jahn-Teller distortion related absorption from ns² to ns¹np¹.²⁹ After Incorporation of Mo³⁺ into the host lattice create new absorption channels around 447 and 538 nm due to spin-

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allowed $d-d$ transition of Mo^{3+} from $^4\text{A}_2$ to $^4\text{T}_2$ and $^4\text{T}_1$ (Figure 2B.3c). Upon doping the separation between two peaks (317 nm and 339 nm) related to Bi^{3+} decreases by 55 meV, as well as relative intensity ratio also changes (inset of Figure 2B.3c), similar observation was also found for Mn^{2+} doping with percentage increment.

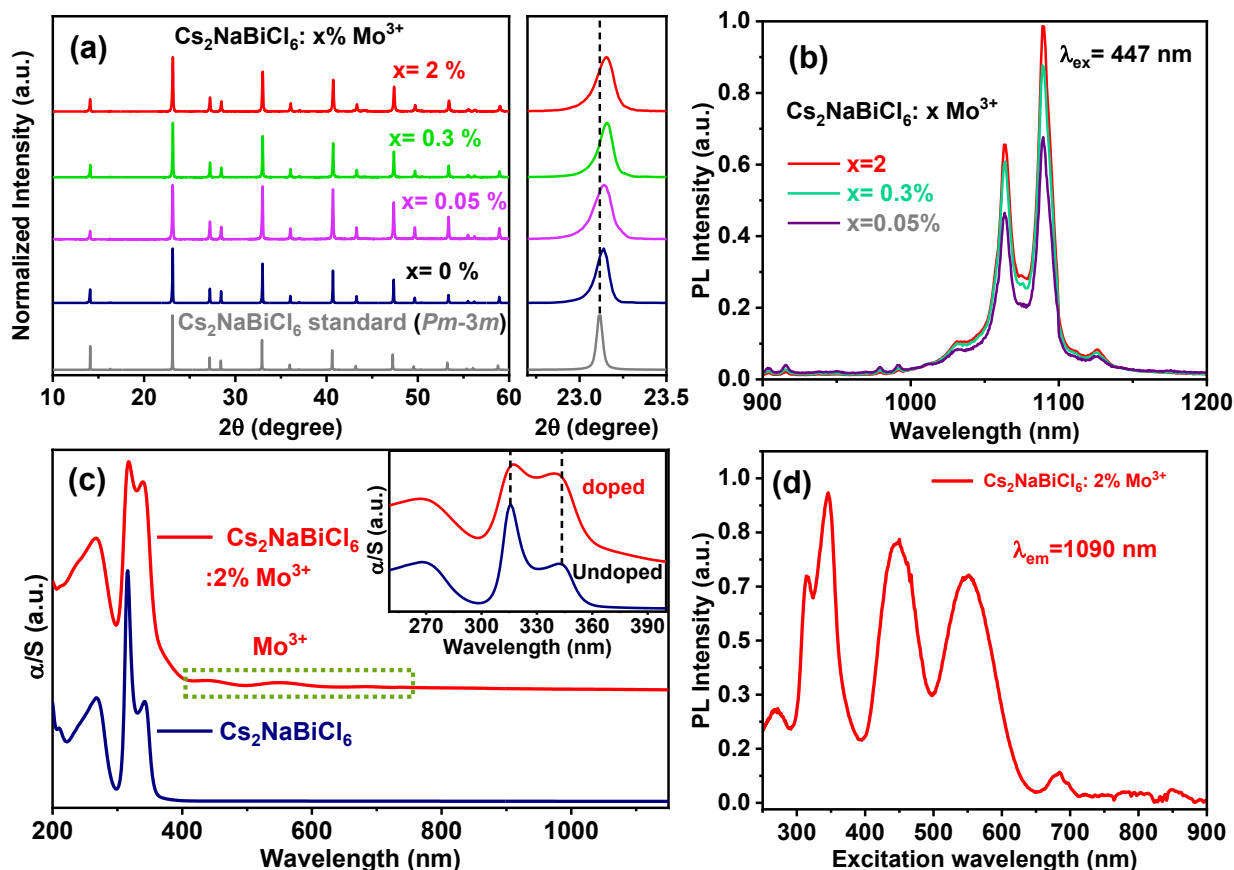


Figure 2B.3: (a) PXRd patterns of undoped and Mo^{3+} doped $\text{Cs}_2\text{NaBiCl}_6$ with different dopant percentages, where, $x = 0.05, 0.3$ and 2 and shift in PXRd peak in magnified view due to smaller ionic radii of Mo^{3+} . (b) Photoluminescence spectra for intensity comparison for different percentages of Mo^{3+} . (c) UV-VIS-NIR absorption spectra comparison of undoped and 2% Mo^{3+} doped $\text{Cs}_2\text{NaBiCl}_6$, the inset shows the difference in Bi^{3+} absorption features in undoped. (black) and 2% Mo^{3+} doped $\text{Cs}_2\text{NaBiCl}_6$ (d) PL excitation spectra of 2% Mo^{3+} doped $\text{Cs}_2\text{NaBiCl}_6$.

Figure 2B.3d, the PL excitation spectra of 2% Mo^{3+} doped $\text{Cs}_2\text{NaBiCl}_6$ well resembles with the absorption in Figure 2B.3c. Along with two spin allowed absorption at 447 nm and 538 nm, there also two spin forbidden $d-d$ transition at 685 nm arises due to Mo^{3+} in corporation. An absorbance corresponding to the emission state comes around 1060 nm which is not visible in the absorption spectra due to low concentration of dopant but can be seen in Mo^{3+} doped $\text{Cs}_2\text{NaInCl}_6$, reported recently.²⁶

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2B.3.2 Temperature-Dependent Structural Phase Transition

Incorporation of dopant, alloying with other element may affect the structural phase transition property of a material, already discussed in previous chapters (section 1.5.1). Figure 2B.4a shows the temperature dependent PXRD pattern of 2% Mo^{3+} -doped $\text{Cs}_2\text{NaBiCl}_6$. At room temperature (298-300 K) $\text{Cs}_2\text{NaBiCl}_6$ process cubic crystal structure and with lowering the temperature, due to shrinkage of unit cell volume the d spacing value of the plane decreases, thereby shifting the peaks towards higher 2θ value. For example, the degenerate peak (222) plane, at 28.52° (shown with dotted like in Figure 2B.4a) shifted to higher 2θ value due to shrinkage of the unit cell as the temperature is lowered. The (400) plane at 33.01° started showing hump like feature at 100 K and get splitted into two different peaks at even lower temperature confirming the phase transition 2% Mo^{3+} -doped $\text{Cs}_2\text{NaBiCl}_6$. The evolution of (400) peak at lower temperature is shown in Figure 2B.4b, where due to c-axis elongation (400) and (040) appears at higher 2θ and (004) appears at lower 2θ following the relation,

For cubic, $a = b = c$ eq (2)

For tetragonal elongation, $c > a, b$ eq (3)

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

So, $d_{(004)} > d_{(400)}$, $d_{(040)}$ and 2θ corresponding to (004) becomes lesser than 2θ value of (400) and (040).

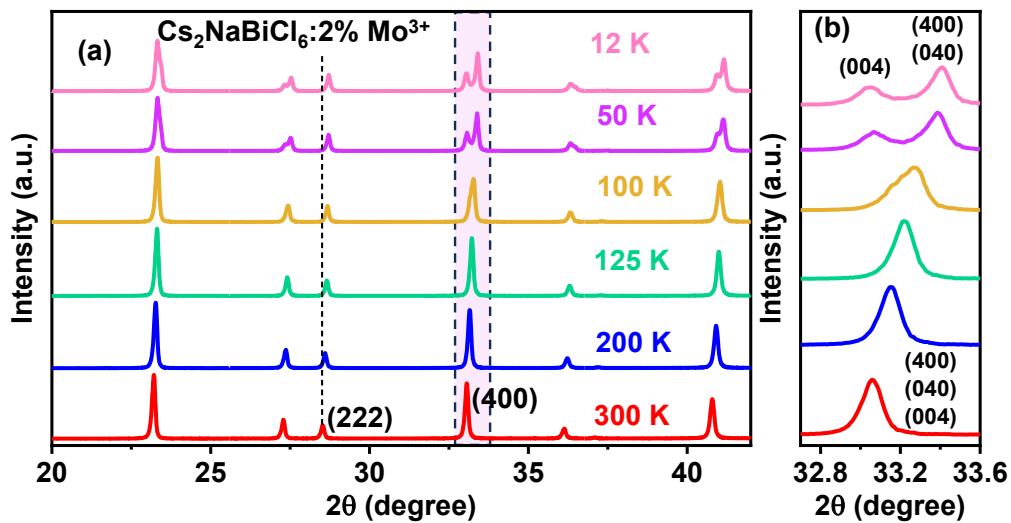


Figure 2B.4: (a) Temperature dependent PXRD pattern of 2% Mo^{3+} doped $\text{Cs}_2\text{NaBiCl}_6$ In the range from 12 to 300 K, highlighted peak showing splitting at lower temperature. (b) Magnified view of same plane with split planes assignment.

2B.3.3 Phase Transition Dependent Optical Properties of Mo^{3+}

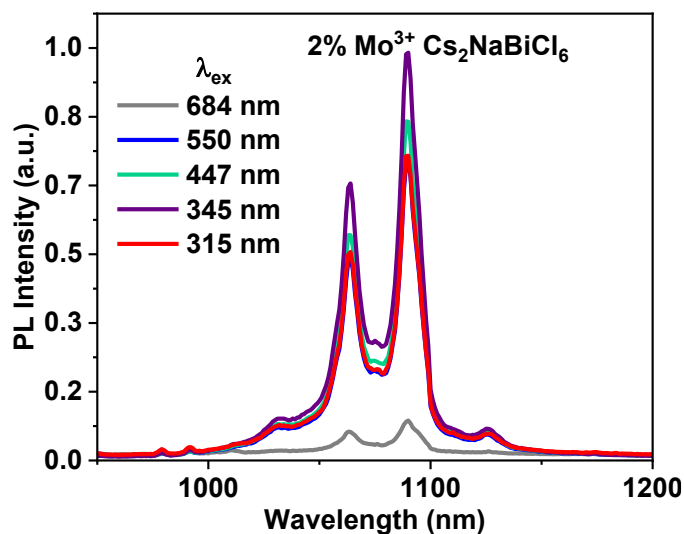


Figure 2B.5: Different excitation wavelength dependent NIR emission of 2% Mo^{3+} -doped $\text{Cs}_2\text{NaBiCl}_6$.

To identify if there is any change in the Mo^{3+} NIR emission due to phase transition, we performed the low temperature photoluminescence experiment. From PL excitation spectra in Figure 2B.3d, it can be understood that Mo^{3+} emission can be obtained by exciting the sample either via Bi^{3+} excitation channel at 315 and 340 nm or Mo^{3+} at 447 and 538 nm. Bi^{3+} can excite Mo^{3+} by energy transfer process by non-radiatively. Exciting the sample at 315 nm gives reasonably good intensity, and the excitation does not change much with temperature, as obtained earlier in chapter 2A in Figure 2A.15b, while the other excitation peak varies with temperature, we keep the excitation fixed at 315 nm throughout the temperature range (300-7 K). Most importantly, exciting the sample either via Bi^{3+} excitation or Mo^{3+} does not lead to any change in Mo^{3+} emission feature other than a little variation in intensity as seen in Figure 2B.5 which well corroborates with the PL excitation data in Figure 2B.d.

From room temperature 300 K to lowest possible temperature around 7 K photoluminescence spectra is shown in 2B.6a. From 300-125 K, the crystal structure should be cubic according to structural characterization discussed in section 2B.3.2. Still in cubic phase at lower temperature, due to crystal shrinkage, as also evidenced from low temperature PXRD shift already discussed, the ligands come closer to metal center. As the halides (Cl^-) comes closer to Mo^{3+} , the crystal field (D_q/B) is expected to increase. According to T-S diagram, an increase in crystal field is expected to increase

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the gap between ground state (⁴A₂) and first excited state (²E). But this increase is very small because of intra-configurational transition and minimal change of octahedra from ground state. Still at lower temperature a blue shift of emission energy is observed in Figure 2B.6a. At 100 K, the cubic to tetragonal transition starts. Below 100 K, a red shift of emission energy is observed. This opposite directionality starting from 100 K is observed for each peak present in emission spectra, like the shoulder peak of 1090 nm, zero-phonon line at 1075 nm and the peak at 1126 nm (Figure 2B.6a-c). The blue shift in cubic structure from 300-100 K for the three peaks at 1090, 1075 and 1126 nm in Figure 2B.6a-c are, 1.7 meV, 0.8 meV and 1.46 meV. Below 100 K the red shift for the same three peaks are 0.8, 0.8 and 1 meV respectively. The blue shift from 300-100 K is explainable for the nearly perfect octahedral geometry around Mo³⁺ following T-S diagram in cubic phase, but tetragonally distorted octahedral geometry may not follow the same T-S diagram, thus the reason of red shift is not clearly understood.

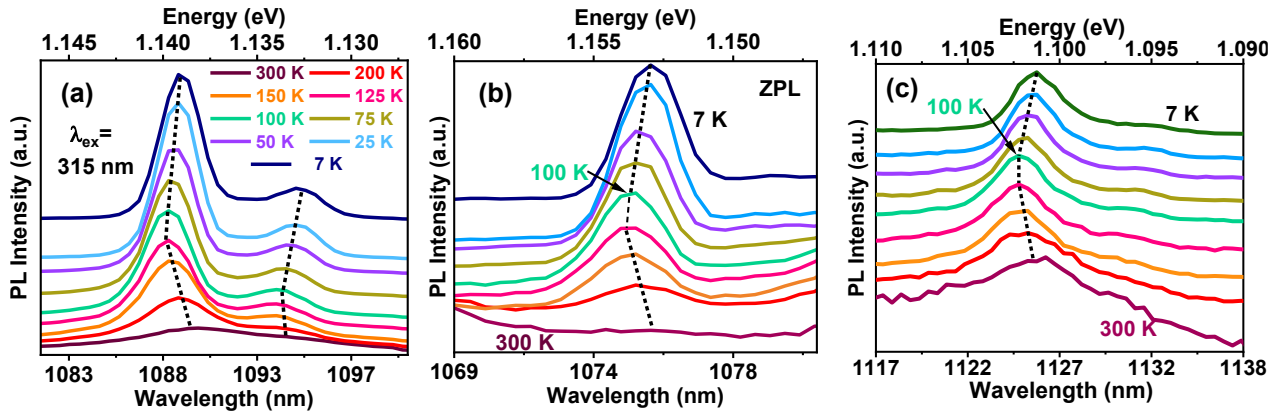


Figure 2B.6: Temperature dependent NIR Photoluminescence spectra from 7-300 K, excited at 315 nm (a) for 1090 and 1095 nm (b) for zero-phonon line at 1075 nm, and (c) for 1126 nm peak of 2% Mo³⁺ doped Cs₂NaBiCl₆.

In contrast, Cs₂NaInCl₆, which retains its cubic phase from room temperature to 7 K, does not show the opposite directional behavior of Mo³⁺ emission.²⁶ So, it is clear due to phase transition from cubic to tetragonal, the opposite directional behavior in emission is observed in Mo³⁺-doped Cs₂NaBiCl₆. So, the anomalous behavior can be attributed to local geometry change of MoCl₆³⁻ but still how the emission process in tetragonally distorted geometry is affected is unknown.

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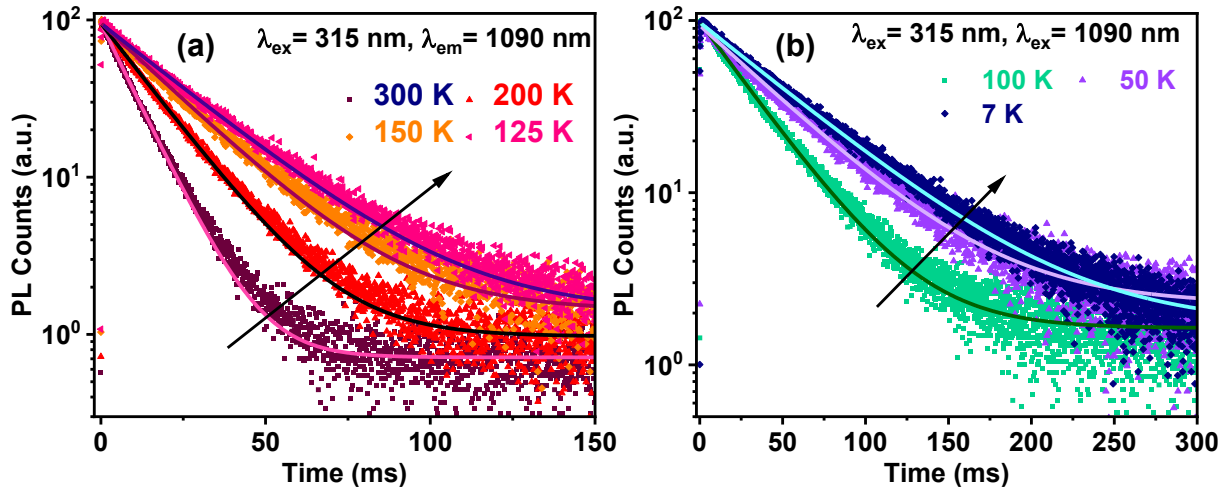


Figure 2B.7: (a) Temperature dependent lifetime of 2% Mo^{3+} doped $\text{Cs}_2\text{NaBiCl}_6$ ($\lambda_{\text{ex}} = 315$ nm, $\lambda_{\text{em}} = 1090$ nm) in cubic phase of $\text{Cs}_2\text{NaBiCl}_6$ from 300-125 K, (b) in tetragonal phase of $\text{Cs}_2\text{NaBiCl}_6$ from 100-7 K. The decays are fitted mono-exponential equation.

Table 2B.1: Temperature dependent fitted values of lifetime of Mo^{3+} emission ($\lambda_{\text{ex}} = 315$ nm, $\lambda_{\text{em}} = 1090$ nm) with flashlamp frequency 2 Hz.

Temperature (K)	Fitted Lifetime (ms) $\pm$ Errorbar	Adj. R-square
300	9.85 ± 0.02	0.99821
250	12.21 ± 0.03	0.99736
200	15.87 ± 0.026	0.99831
175	18.40 ± 0.02	0.99868
150	21.53 ± 0.04	0.99742
125	25.92 ± 0.04	0.99716
100	32.46 ± 0.05	0.99761
75	40.00 ± 0.08	0.99558
50	48.09 ± 0.10	0.99600
25	53.20 ± 0.08	0.99772
7	55.33 ± 0.09	0.99758

Lifetime of an emission process describes the excited state decay dynamics. Figure 2B.7a and b shows decay profile of 1090 nm emission excited with 315 nm energy, of MoCl_6^{3-} moiety in cubic and tetragonal $\text{Cs}_2\text{NaBiCl}_6$ respectively. Being both Laporte and spin forbidden transition from ^2E to $^4\text{A}_2$, the lifetimes remain in millisecond range. At lower temperature due to suppression of nonradiative decay channels the radiative lifetime at excited state usually increases (black arrows in Figure 2B.7a and

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b). At lower temperature lifetime increases by 5-6 folds as found by fitting the decay profile in monoexponentially component. The fitted values from 300-7 K are tabulated (Table 2B.1). The lifetime increases gradually like the same way, in $\text{Cs}_2\text{NaInCl}_6$ host reported recently.²⁶

Below 175 K, another emission in visible range, ~695 nm with multiple side bands start to come (Figure 2B.8a) violating the Kasha's rule. This peak is assigned as emission from second excited state, 2T_2 to 4A_2 (see T-S diagram in Figure 2B.2a).²⁴⁻²⁶ The appearance of this emission is strictly not related to phase transition because the appearance of emission at temperature 175 K is far higher than the phase transition temperature (~100 K). Interestingly, unlike the NIR emission in Figure 2B.6, no anomalous behavior of this emission upon phase transition is observed. Peak position remains almost same, only small enhancement in intensity due to temperature effect is observed. This visible emission peak has FWHM as low as 5-6 meV like the NIR emission around 1090 nm. So, it can be concluded that this peak not showing discontinuity in peak position like the NIR emission, cannot be attributed to the its FWHM since for both emissions they are comparable. Since this transition is also spin and Laporte forbidden, the lifetime appears at arrange of sub-millisecond which enhances further towards 7 K due to suppression of non-radiative decay (Figure 2B.8b).

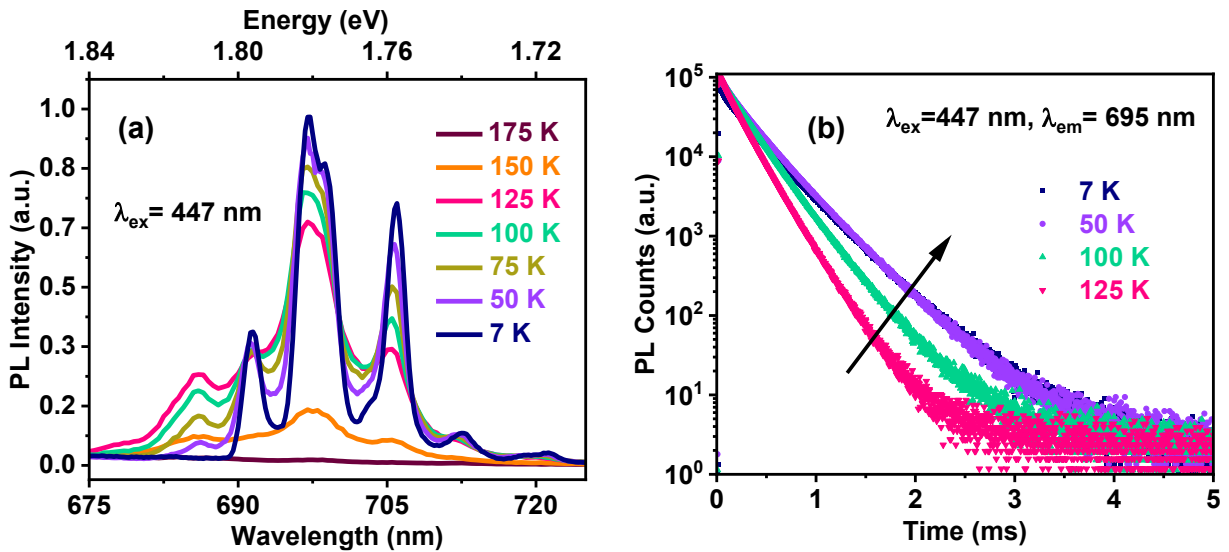


Figure 2B.8: (a) Temperature dependent PL emission and (b) lifetime from 2T_2 state to ground state, 4A_2 , excitation wavelength= 447 nm for 2% Mo^{3+} doped $\text{Cs}_2\text{NaBiCl}_6$.

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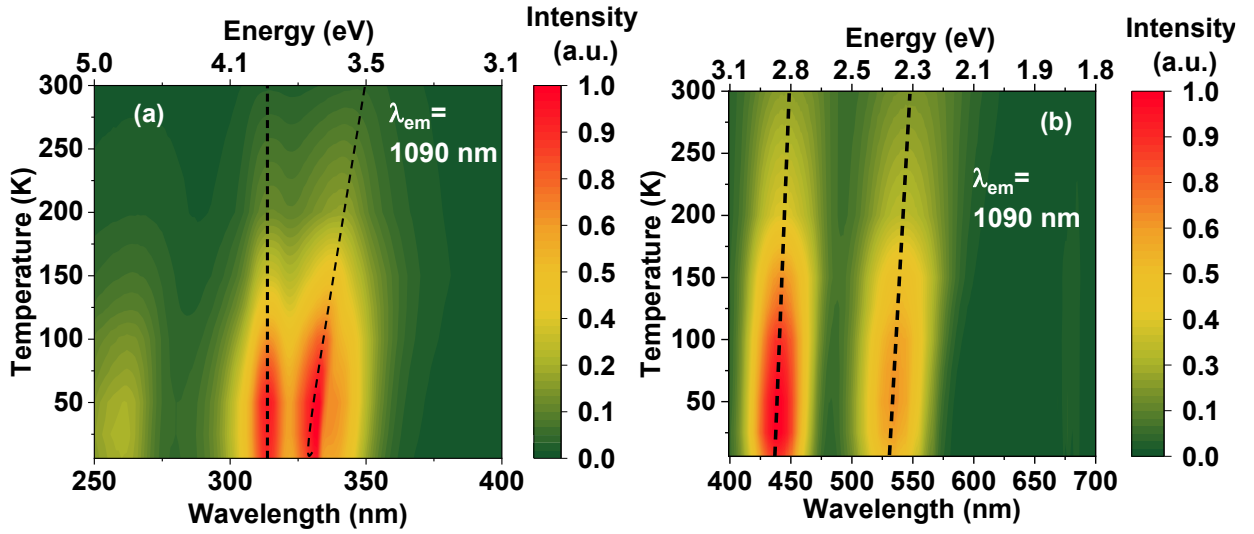


Figure 2B.8: Temperature dependent 3D contour colormap of PL excitation at (a) Bi^{3+} and (b) Mo^{3+} absorption, emission wavelength fixed at 1090 nm from 300-7 K.

The PL excitation spectra represent the absorbing states responsible for an emission to occur. As also shown in Figure 2B.3d, both Bi^{3+} absorption channels (Jahn-Teller distortion allowed $\text{ns}^2 \rightarrow \text{ns}^1\text{np}^1$ at 316 and 339 nm) and Mo^{3+} ($^4\text{A}_2 \rightarrow ^4\text{T}_2$ at 538 nm and $^4\text{A}_2 \rightarrow ^4\text{T}_1$ at 447 nm) are responsible for Mo^{3+} emission from lowest excited state ^2E to ground state $^4\text{A}_2$. The temperature dependent evolution of these Bi^{3+} and Mo^{3+} related absorption giving Mo^{3+} emission is shown in Figure 2B.8a, b. Due to crystal structure change, likewise emission, the absorption may get affected by the local geometry change of Bi^{3+} and Mo^{3+} octahedra to tetragonally distorted one. But no such observation was there. The trends in absorption or excitation peak are shown with black dashed lines in both the Figures 2B.8a and b. The separation between dynamic Jahn-Teller distortion of Bi^{3+} decreases at lower temperature (Figure 2B.8a).³⁰ The regular trend is followed as an effect of temperature and no discontinuity is observed around 100 K due to phase transition. Similarly, for Mo^{3+} two absorption peaks follow temperature dependent trend that, at lower temperature with increase in crystal field (D_q/B), the two absorptions, $^4\text{A}_2 \rightarrow ^4\text{T}_2$ and $^4\text{A}_2 \rightarrow ^4\text{T}_1$ will be blue shifted towards higher energy parallelly according to T-S diagram of d^3 system (blue and green line in Figure 2B.2a). One of the probable reasons why these peaks do not show abrupt change due to phase transition may be due to higher FWHM. The absorption peaks of Bi^{3+} , have FWHM of around 150 meV. FWHM for Mo^{3+} at 447 and 538 nm are 430 and 372 meV respectively. Such huge FWHM may suppress the phase transition effect. In contrast, a transition with 5-6 meV also did not show phase

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transition effect (emission at 694 nm). Only the opposite directionality due to local structural change is observed in NIR emission but still the impact on the emission process yet to be understood.

2B.4 Conclusions

The global phase transition of Cs₂NaBiCl₆ from cubic to tetragonal changes local geometry of doped Mo³⁺ in octahedral coordination. Though the local structural information of MoCl₆³⁻ from nearly perfect octahedra to tetragonally distorted octahedra yet not evidenced, but the narrow NIR photoluminescence of Mo³⁺ shows anomalous behavior before and after phase transition. In cubic phase the emission shows blue shift from 300-100 K owing to the ligands coming closer enhancing crystal field maintain nearly octahedra with six halides. But below the emission shows red shift, clearly indicating not a similar geometry is maintained like cubic structure. A tetragonal distortion of MoCl₆³⁻ is expected, but how the excited state giving emission is affected, is not yet understood. The other emission from second higher excited state does not have an impact of phase transition despite having narrow FWHM.

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Note: Temperature dependent Raman spectra discussed in this chapter were measured by Aprajita Joshi and Dr. Surajit Saha in IISER Bhopal.

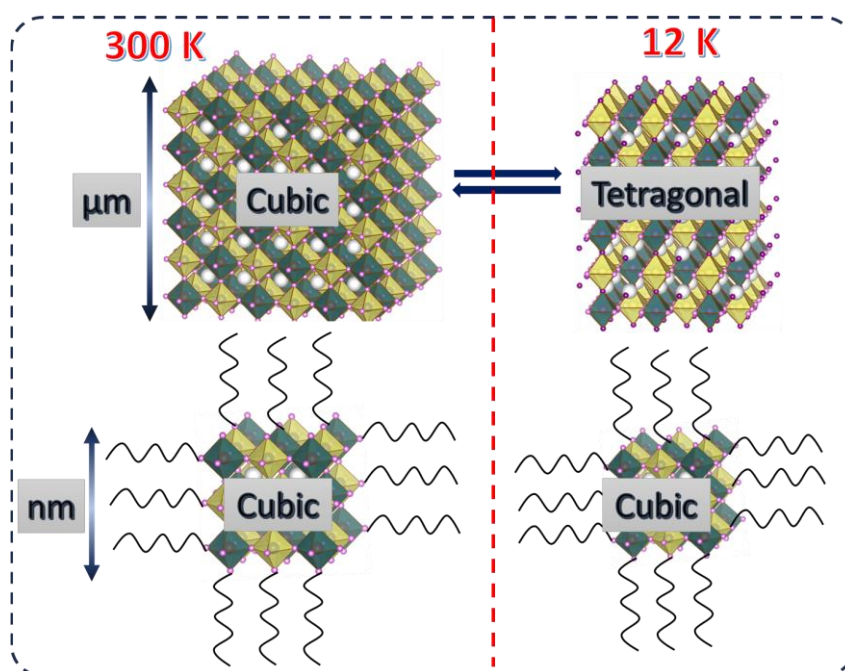
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Temperature Dependent Phase Transition in $\text{Cs}_2\text{NaBiCl}_6$ Nanocrystals: Size Effect

Abstract

Bulk (micro-meter sized crystals) $\text{Cs}_2\text{NaBiCl}_6$ shows temperature dependent phase transition from cubic to tetragonal below 110 K by elongation along one dimension out of three and rotation of unit cell. But when the crystallite size reduces to a few tens of nanometre ($\sim 10\text{-}20\text{ nm}$), it remains in cubic phase throughout the temperature range from 300-12 K. Lattice parameters and local vibrational modes are probed by temperature dependent X-ray diffraction and Raman spectroscopy as indicating parameters to phase transition. We attribute this deviation in phase transition behavior to the increase in surface to volume ratio as we go from bulk to nanocrystals. This enhancement in surface to volume ratio enhances surface energy contribution to the total energy and thermodynamically restricts the process of phase transition for nanocrystals to occur. Also, another difference arises in the surface termination, bulk terminates with the uncoordinated dangling bonds surrounding Cs^+ , Na^+ , Bi^{3+} or Cl^- , while in case of nanocrystals, the uncoordinated bonds are partially passivated with organic capping ligands. The capping ligands also may have an impact on restricting the phase transition property in nanocrystals.

Graphical Abstract



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3.1 Introduction

Metal halide perovskites often change their crystal structure based on external conditions like temperature and pressure.¹ The importance of this change in crystals structure is enormous. Different crystal structures have different electronic band structure thereby affecting the optical properties, optoelectronic device performance (solar cell, LEDs), and dielectric property. For example, bulk cesium lead iodide (CsPbI₃) perovskite has bandgap of 1.26 eV, 1.70 eV and 2.0 eV in cubic (α), tetragonal (γ) and orthorhombic (β) phases.² The cubic one having the lowest bandgap is ideal for solar cell or LEDs among the other semiconducting polymorphs. But the cubic phase is stable only above 360 °C and converts to its non-semiconducting δ -phase at room temperature which cannot be used in solar cell or LEDs.³⁻⁵ This conversion from unstable semiconducting α -phase to stable non-semiconducting δ -phase at room temperature is partially suppressed when the crystallite size of CsPbI₃ is reduced to a few nanometers (from ~3 - 50 nm). Though the stability of CsPbI₃ NCs (at least stable up to 2 days) is anyway more than bulk in cubic phase at room temperature, for NCs removal of unreacted species and excess ligands to an optimum extent makes the stability difference from 2 days to 60 days and here comes the role of surface treatment.⁶ Thus, not only size, the role of surface ligands also may be responsible for stabilizing one phase or restricting the transformation to other phase.

In addition to the size and surface ligand effects, there are examples of lattice doping influencing the structural phase transition. For example, CsPbI₃ bulk stability can be enhanced by doping 4% Bi³⁺.⁷ Also, Cs(Pb/Sn)I₃ alloyed NCs show stability up to 150 days in ambient condition.⁸ This restriction of phase transition is not only restricted within the halide perovskite, but also observed in other kind of perovskites like BaTiO₃. In BaTiO₃, the crystal structure change from cubic to tetragonal to orthorhombic can be suppressed by a partial (20%) replacement or alloying of Ba²⁺ by Ca²⁺.⁹ So, this is very general observation that changing the composition by doping or alloying may preferably stabilize one phase over other as compared to undoped or unalloyed host.

In chapter 2, we discussed Cs₂NaBiCl₆ double perovskite that undergoes cubic to tetragonal phase transition when the temperature is lowered below ~110 K. This

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phase transition property was not altered by doping a few % Mn²⁺, suggesting that it is not necessary that all dopants do not influence the phase transition in a similar way.¹⁰ In a similar way, doping a small amount of Ag⁺ in Cs₂Na_{0.95}Ag_{0.05}BiCl₆ shows cubic to tetragonal phase transition below ~90 K, similar to the undoped Cs₂NaBiCl₆.¹¹ Also changing halide counterpart completely from Cl⁻ to Br⁻, doesn't alter cubic to tetragonal transition behavior in Cs₂AgBiBr₆, but the transition temperature changes to ~122 K.¹² Based on the above example, it appears that the minor compositional changes do not significantly alter the phase transition properties of Cs₂B'BiX₆ type of double perovskite where B' is a monovalent metal center and X is Cl/Br.

But without changing any composition like doping or alloying, the phase transition property of same Cs₂NaBiCl₆ crystal is ceased when the size of the crystal is brought down to a few nanometers scale. Similar observation has already been there for plenty of materials, BaTiO₃,¹³ PbTiO₃,¹⁴ CH₃NH₃PbBr₃,^{15, 16} as also the one like discussed above for CsPbI₃. Generally, it has been observed that, as the crystallite size decreases, the phase transition temperature (T_c) decreases, or it disappears completely, indicating that the phase transition process is unfavorable for smaller nanometer sized crystals as compared to their bulk counterpart. This indicates that, the high temperature phase for bulk is stabilized at lower temperature in NCs. The main determining parameter for this unfavorable process is, the high surface energy contribution of NCs to the thermodynamic parameters, like enthalpy, entropy and Gibb's free energy that determines spontaneity of a process to occur and the surface termination with the passivating ligands. Whereas, in case of bulk, the core part dominates over the surface.

3.2 Experimental Section

3.2.1 Chemicals

Cesium acetate (CsOAc, ≥99.9%), sodium acetate (NaOAc, ≥99.0%), bismuth acetate (Bi (OAc)₃, ≥99.99%), Trimethylsilyl chloride (TMSCl, ≥98.0%), 1-octadecene (90%,), oleylamine (>98%,), oleic acid (90%,), hexane (≥97%,) are purchased from Sigma Aldrich chemicals. All the chemicals have been used without further purification.

3.2.2 Synthesis of $\text{Cs}_2\text{NaBiCl}_6$ Nanocrystals

Colloidal $\text{Cs}_2\text{NaBiCl}_6$ nanocrystals have been synthesized using hot-injection method as schematically shown in Figure 3.1. 0.355 mmol CsOAc , 0.25 mmol NaOAc , 0.25 mmol $\text{Bi}(\text{OAc})_3$ were dissolved in 1.4 ml oleic acid (OA), 0.3 ml Oleylamine (OLAm) and 5 ml 1-octadecene (ODE) and heated to 120 °C under N_2 flow. Then the reaction mixture was kept under vacuum for half an hour. Then under N_2 flow the reaction mixture was heated to 145 °C. Then 0.18 ml of TMSCl was injected and the reaction was continued for 10-20 seconds. The reaction mixture became turbid off-white in color and then quenched with ice-water bath and cooled down to room temperature. The mixture was centrifuged at 7830 rpm (revolution per minute) for 20 minutes to extract the formed nanoparticles. The supernatant was discarded and precipitate was dispersed in 5 ml hexane. The dispersion was centrifuged again at 3000 rpm for 5 minutes and the transparent colourless supernatant was collected and stored for further experiment.

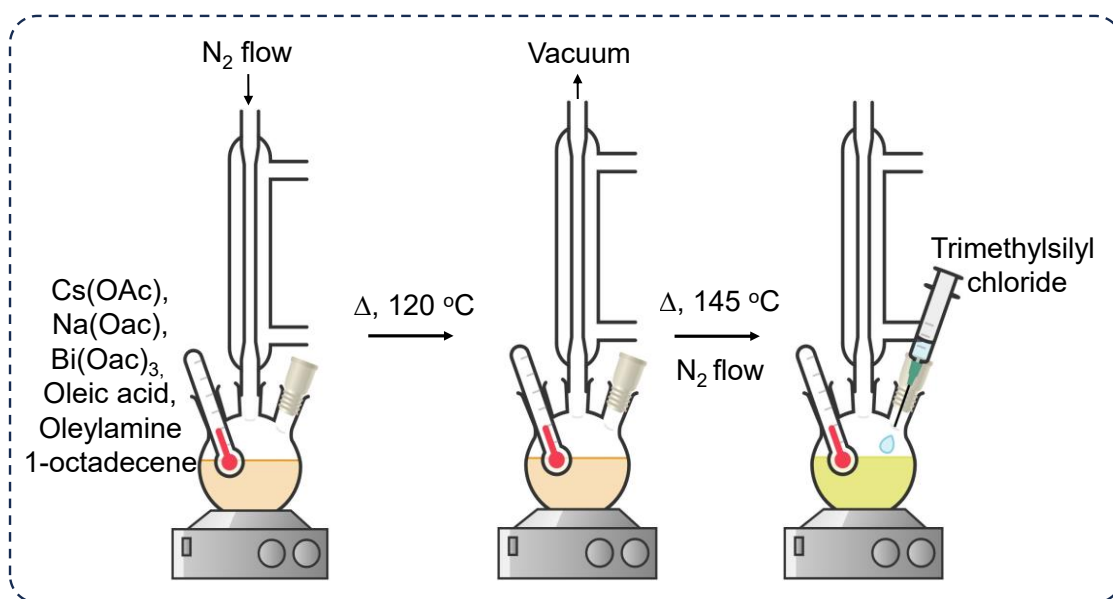


Figure 3.1: Schematic presentation of reaction procedure for the synthesis of colloidal $\text{Cs}_2\text{NaBiCl}_6$ nanocrystals.

3.2.3 Characterization

Temperature dependent powder XRD patterns are measured in a wide temperature range of 15 to 300 K using a Malvern Panalytical Empyrean Series-III X-

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ray diffractometer equipped with Cu K α radiation (1.54 Å) and a 1Der strip detector. The step size of 2 θ was 0.008°, and the counting time was 2 s per step. The XRD sample of NCs was prepared by drop-casting the colloidal hexane dispersion NCs on flat metal holder. UV-visible absorption spectra were recorded using a Perkin Elmer, Lambda-45 UV/Vis spectrometer. LabRAM HR Evolution Raman spectrometer coupled with attoDRY S3 1000 He cryostat and attached to a Peltier-cooled charge-coupled device (CCD) detector. Raman spectra are collected by illuminating the samples with 532 nm (green) laser excitation sources. For bulk, pellet was made for Raman measurement and for nanocrystals dispersion was drop cast on Silicon wafer.

3.3 Results and Discussion

Both bulk and nanocrystalline Cs₂NaBiCl₆ crystallize in cubic structure (*Fm-3m*) at room temperature as shown by the powder XRD patterns in Figure 3.2a. Peak position remain same in both the systems while the relative intensities vary. In the case of bulk, it overall follows the simulated data (bottom most, grey coloured), while the nanocrystal has (400) plane as the most intense one, in difference with bulk. For spherical particles, drying them to form a powder randomly orients them on substrate, and there is a statistically random distribution of crystal plane orientations with respect to the diffraction angle. As particle shapes become nonspherical (as mostly reported for Cs₂NaBiCl₆ is cube shaped),¹⁷⁻¹⁹ there is a chance that, they will orient in non-random directions. They will tend to orient with their flat faces parallel to the drying surface. It is much less likely that nanotubes would dry with their corners or edges touching the drying surface, and therefore, the powder of nanocubes will be preferentially oriented in the crystallographic direction corresponding to the faces.²⁰ In our system, the intense peak for (400) plane might be due to the preferred orientation along that direction. But due to cube shape not significantly higher than the other planes

In Bulk, the grinded powdered samples are also randomly oriented, that is expected to deviated from relative intensity order from standard or single crystal pattern. But this is not the case because each micrometre sized-particle has enough long-range ordering of a particular plane similar to single crystal. So, all the planes are equally exposed to the diffraction beam source and detector, while not grinding the

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crystal well may not lead to preferred orientation like NCs but unequal or selective exposure of few planes shown relative intensity deviation from standard pattern.

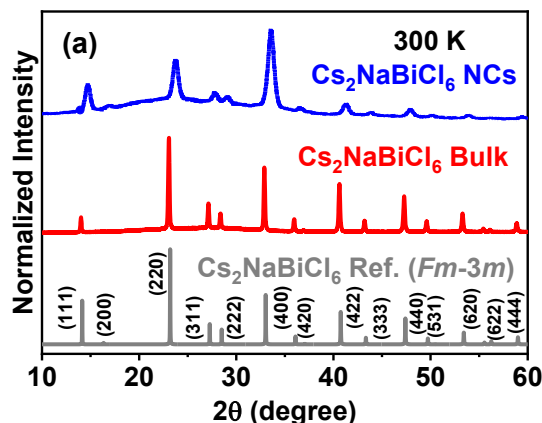


Figure 3.2: (a) Powder XRD patterns of bulk (red) and nanocrystal (blue) samples compared with the standard pattern of cubic $\text{Cs}_2\text{NaBiCl}_6$ at room temperature.

The broadening in powder XRD pattern of nanocrystals arises mainly due to the size effect.²⁰ To obtain of the crystallite size of our NCs, we use Debye Scherrer equation,²¹

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (3.1)$$

where, D = crystallite size, k is shape factor, nearly unity, λ is X-ray wavelength, β is full width half maxima of the peak expressed in radian, and θ is Bragg angle and the obtained size. The obtained size of our $\text{Cs}_2\text{NaBiCl}_6$ NCs is approximately 12 nm.

As the crystallite size falls within a range where size effect is dominant over instrumental broadening, the peak broadening can be related to the inherent crystallite properties. Scherrer equation only explains the effect of crystallite size, hence, point defects, stacking faults are not taken into account.

From the digital image in Figure 3.3 (left side column), bulk $\text{Cs}_2\text{NaBiCl}_6$ having size in order of micro to millimetre scale are not dispersible in solvents. While due to nanometre size (~ 12 nm) and with the help of capping ligands like oleic acid and oleylamine, nanocrystals are dispersible in organic nonpolar solvents and make transparent solution (right side column). Subsequently, one can make a film of nanocrystals by drop casting upon evaporation of volatile solvents, for example, here

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the solvent is hexane. Among many volatile solvents hexane has been used as it is nonpolar in nature and does not wash the capping ligands out.

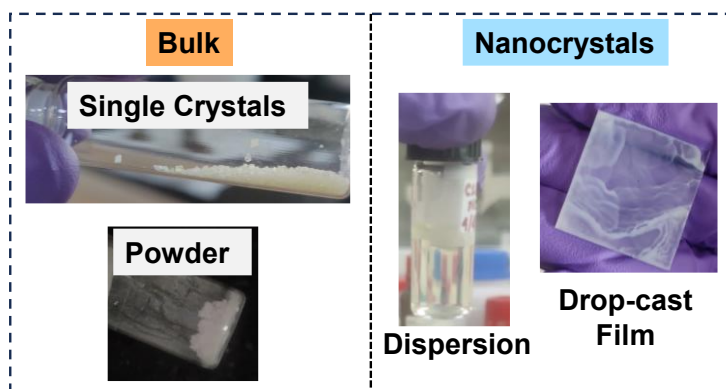


Figure 3.3: Left side: Digital image of bulk $\text{Cs}_2\text{NaBiCl}_6$ crystals in powder form. Right side: colloidal $\text{Cs}_2\text{NaBiCl}_6$ nanocrystals in hexane and its drop cast film on glass substrate.

3.3.1 Temperature-Dependent Global Structure: Bulk and Nanocrystals

The phase change of bulk $\text{Cs}_2\text{NaBiCl}_6$ is evident from the powder XRD pattern where three degenerate peaks in cubic space group ($Fm-3m$) (Figure 3.4, red pattern) split into two peaks with nearly 2:1 intensity ratio in tetragonal space group ($I4/mmm$) (Figure 3.4, orange pattern). This phase transition has been discussed in detail in chapter 2A. But for $\text{Cs}_2\text{NaBiCl}_6$ nanocrystals the lowest temperature (12 K) powder XRD (sky curve) does not split and remain similar to that of cubic phase pattern (blue curve) observed at 300 K.

It is difficult to comment on the splitting because of the large FWHM of the nanocrystals' powder XRD peaks. Even the split peaks of bulk (orange curve in Figure 3.4) come within the range of FWHM of a single peak of NCs (both blue and sky). But a closer look at change in FWHM of bulk and NCs at room and lowest temperature can rule out the phase transition or splitting as probable reason for peak broadening. At room temperature bulk (red curve in Figure 3.4) has FWHM of 0.085° while FWHM for NCs is 0.68° corresponding to one single plane, (400) plane around 33° . This difference in Full width half maxima (FWHM) is predominantly because of huge size difference between the bulk and nanocrystal.

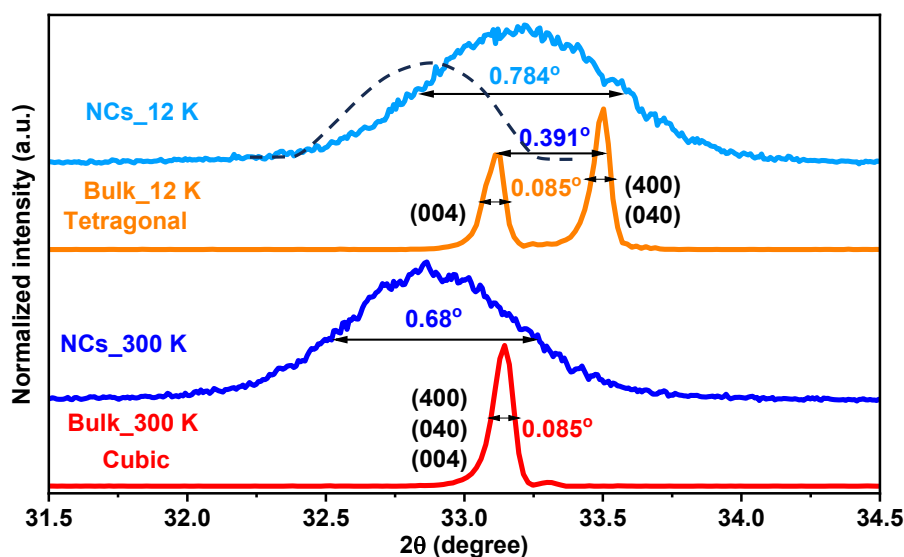


Figure 3.4: Powder XRD patterns of $\text{Cs}_2\text{NaBiCl}_6$ at 300 K for bulk (red curve), NCs (blue curve) and 12 K for bulk (orange curve) and NCs (sky blue).

At lower temperature the FWHM for bulk corresponding to one peak, say, (400) or (040) plane at 33.502° is remaining similar to that of room temperature (0.085°). But a separate peak appears at lower $2\theta = 33.111^\circ$ for (004) plane in tetragonally elongated phase which has similar FWHM of 0.085° . The separation between these two peaks for bulk is 0.391° . Since split peak have different intensity of 2:1 ratio (orange line), we expected a separated hump or shoulder peak for nanocrystal which might appear to be like the dotted black line (on sky blue curve). No such signature was observed for NCs at even lowest temperature signifies there is no peak splitting or phase transition for NCs.

Figure 3.5a shows colormap of full range powder XRD patterns for nanocrystals from 300 - 12 K. No signature of peak splitting or shoulder peak or hump is observed in the entire temperature range. At lower temperatures, a continuous shift of peak towards higher 2θ is observed which is regular temperature dependent phenomena. This shift is observed for both bulk and nanocrystal samples because of the shrinking of unit cell at lower temperature. But for bulk $\text{Cs}_2\text{NaBiCl}_6$, the interlayer distance (d) along a, b and c axis become different below 110 K (Figure 3.5b, red circles) due to tetragonal elongation, while the NCs show monotonous decrease (blue diamonds) in d spacing with decreasing temperature.

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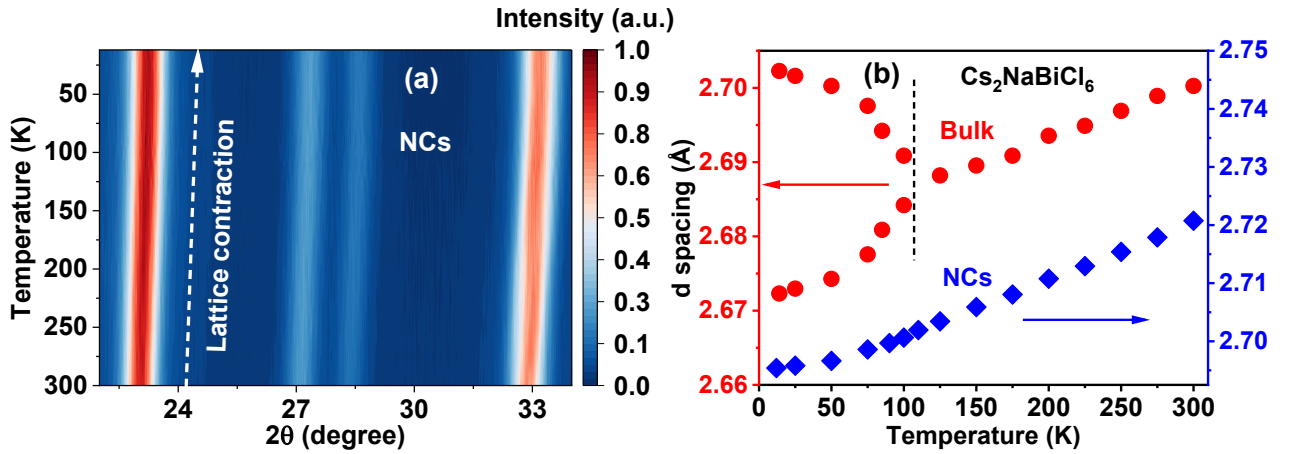


Figure 3.5: (a) 3D contour plot of powder XRD patterns of $\text{Cs}_2\text{NaBiCl}_6$ NCs at different temperatures from 300-12 K. (b) Interlayer spacing, d , corresponding to (400) plane for $\text{Cs}_2\text{NaBiCl}_6$ bulk (red circles) and NCs (blue diamonds).

As we can see in Figure 3.5b, the d spacing decreases linearly from 300 to 50 K in case of NCs, but the decrease is not linear below 50 K to 12 K. For Bulk such observation is not made since the d spacing becomes nondegenerate due to phase transition still the linearity is maintained at least from 300 to 110 K in cubic phase. The decrease is expected to be linear because the thermal expansion or compression coefficient is defined by,

$$\Delta l = l \times \alpha \times (T_i - T_o) \quad (3.2)$$

where, Δl is extent of expansion or compression between two temperatures, l is length at initial temperature, α is thermal expansion coefficient, T_i final temperature, T_o is initial temperature. Although at lower temperature the contraction along a , b axes decreases and also expansion of c axis decreases, the expansion and contraction are nonlinear and saturates near 0 K. Since the contraction happens due to decrease in bond length, up to a certain temperature they come to the closest possible positions and the bond length contraction saturates at very low temperatures near 0 K.²² Thereby, both bulk and NCs of $\text{Cs}_2\text{NaBiCl}_6$ below 20 K shows such saturation deviating from the linear trend. This deviation from lattice contraction near 0 K is not any unique property indicating phase transition at that point, but this observation is very general and have been there for the systems not undergoing a phase transition.²³⁻²⁵

3.3.2 Temperature-Dependent Raman Spectroscopy: Bulk and Nanocrystals

Raman modes of octahedra become different in different phases like cubic and tetragonal. Therefore, we employed temperature dependent Raman spectroscopy to probe the possibility of temperature dependent phase transition in bulk and nanocrystals of $\text{Cs}_2\text{NaBiCl}_6$. Furthermore, unlike XRD patterns, the FWHM of Raman spectra of bulk and NCs of $\text{Cs}_2\text{NaBiCl}_6$ are similar (Figure 3.6a), which might become helpful to distinguish the possible phase transition.

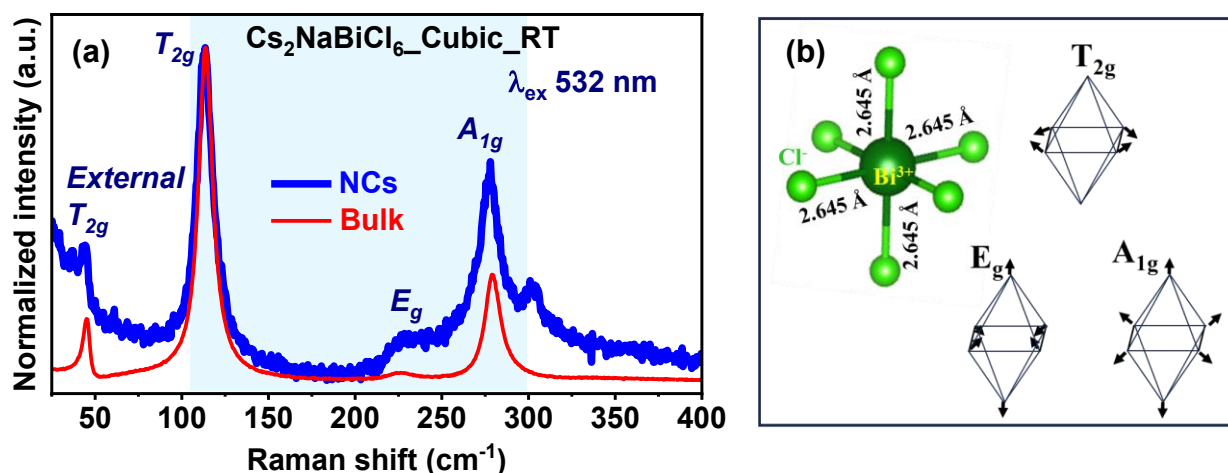


Figure 3.6. (a) Room temperature Raman spectra of $\text{Cs}_2\text{NaBiCl}_6$ bulk (red spectra) and NCs (blue spectra) (b) Associated vibrational modes from BiCl_6^{3-} octahedra.

In cubic system there are four Raman modes coming from three irreducible representation, those are $2 \times T_{2g} + E_g + A_{1g}$. The first peak appears at around 46 cm^{-1} in Figure 3.6a, which is attributed to Cs^+ translational motion that is isotropic at three dimensions in space between $[\text{NaCl}_6]^{5-}$ and $[\text{BiCl}_6]^{3-}$ octahedra at room temperature.^{10, 26-28} This motion is corresponding to external T_{2g} mode of Cs^+ ions for both bulk and NCs of $\text{Cs}_2\text{NaBiCl}_6$. The rest of three peaks around 114, 226 and 278 cm^{-1} come from internal octahedral breathing modes, T_{2g} , E_g and A_{1g} respectively, that are depicted in Figure 3.6b.²⁹ These three modes are attributed to $[\text{MCl}_6]^{n-}$ ($\text{M} = \text{Bi}/\text{Na}$) octahedra as previously assigned in literature.¹⁰ Also metal halide based perovskites forming shared MCl_6^{n-} octahedral units show similar Raman vibrational modes at similar frequency range.³⁰ These three modes follow the relation (sky blue shaded area in Figure 3.6a) from octahedra follows the relation,^{28, 31-33}

$$A_{1g}^2 = E_g^2 + \frac{3}{2} T_{2g}^2 \quad (7)$$

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A perfect octahedra in ground state belongs to O_h symmetry with equal six bond lengths. When it undergoes tetragonal distortion (expansion or compression) the symmetry becomes D_{4h} . The triply degenerate T_{2g} mode in cubic phase decomposes to doubly degenerate E_g and nondegenerate B_{2g} modes.³⁴ As seen in Figure 3.7, the Raman spectra of $\text{Cs}_2\text{NaBiCl}_6$ bulk at 300 K in cubic phase has four peaks at 46, 112, 231 and 284 cm^{-1} . But at lowest temperature (10 K), the T_{2g} peak around 112 cm^{-1} show one shoulder peak (navy blue curve). This is because of the lifting of degeneracy of T_{2g} mode. Alongside the external T_{2g} mode corresponding to Cs^+ translational motion which was isotropic in all three dimensions in cubic phase, becomes anisotropic in tetragonal phase. So, this peak starts to become asymmetric around 105 K (just below the phase transition temperature), and splits into two separate peaks (the star marked peaks in Figure 3.7) at further lower temperatures. On the contrary, the non-degenerate A_{1g} mode, corresponding to symmetric stretching of all six metal halide bonds in three dimensions, at around 284 cm^{-1} remains as a single peak throughout the temperature range from 300-10 K irrespective of cubic or tetragonal crystal structure. The E_g being double degenerate is also expected to split in two peaks, A_{1g} and B_{1g} .³⁵ But due to very less intense signal it is difficult to observe the splitting (see the enlarged view of E_g peak evolution from 300-10 K in Figure 3.8).

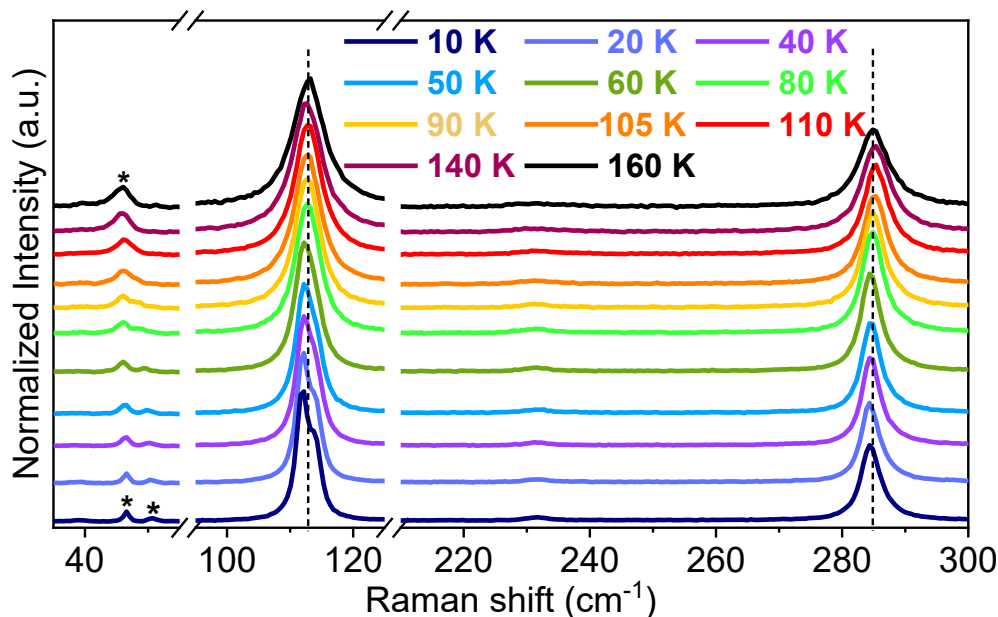


Figure 3.7. Temperature dependent Raman spectra of bulk $\text{Cs}_2\text{NaBiCl}_6$ (pellet) in the temperature range of 160-10 K.

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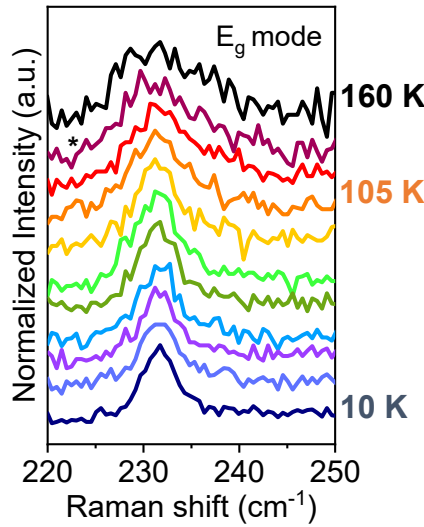


Figure 3.8. Temperature dependent E_g mode Raman spectra of bulk $\text{Cs}_2\text{NaBiCl}_6$ (pellet) in the temperature range of 160-10 K (enlarged view from Figure 3.7)

In all above-mentioned Raman modes, the FWHM of the peaks decreases as the temperature decreases. This is due to the decrease of lattice vibrations at lower temperatures, or less phonon-phonon scattering thereby increasing phonon mean free path. As the phono-phonon scattering decreases the lifetime of phonons that is the time at excited state prolongs at lower temperature. Assuming Raman peak to be Lorentzian in nature FWHM is related to phonon following the equations,³⁶

$$\Delta t = \frac{1}{\pi c \Gamma} \quad (3.3)$$

where Δt lifetime, c is velocity of light, Γ is FWHM. Or we can say from uncertainty principle that FWHM is the uncertainty in energy, thus

$$\Delta E \times \Delta t = \frac{\hbar}{2} \quad (3.4)$$

where ΔE is uncertainty in energy (FWHM), $\hbar$ is reduced Planck constant. The peak does not come as a sharp line rather as a Lorentzian distribution, indicating not a single value of E but there is uncertainty, designated by ΔE increasing the FWHM. Δt increases at lower temperatures decreasing ΔE , and thereby lowering the FWHM.

Unlike bulk samples (Figure 3.7), the $\text{Cs}_2\text{NaBiCl}_6$ NCs (Figure 3.9) do not splitting of T_{2g} modes at $\sim 113 \text{ cm}^{-1}$ below 105 K. A single peak has been observed

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throughout the temperature range of 160 - 10 K has been observed (Figure 3.9). This observation suggest the absence of tetragonal elongation or compression inside octahedra along one axis for the nanocrystals. Consequently, the Raman spectra suggest absence of cubic to tetragonal phase transition of $\text{Cs}_2\text{NaBiCl}_6$ NCs in the entire temperature range of 300-10 K. This finding from Raman spectroscopy corroborates with the temperature dependent XRD results discussed in the previous subsection.

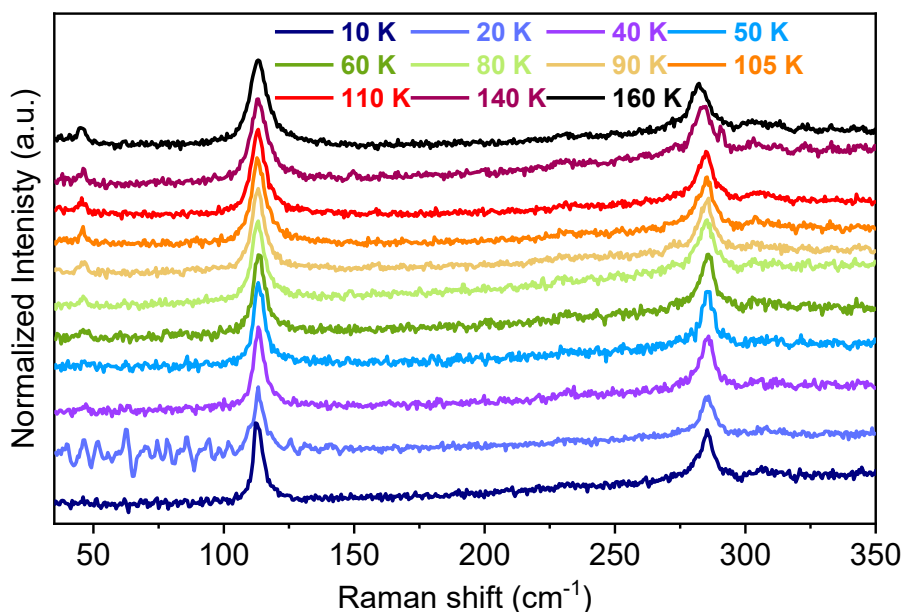


Figure 3.9. Temperature dependent Raman spectra of $\text{Cs}_2\text{NaBiCl}_6$ NCs film on Silicon wafer in the temperature range of 160-10 K.

Figure 3.10 shows the Raman spectrum of $\text{Cs}_2\text{NaBiCl}_6$ NCs film over an extended range of wavenumber covering both inorganic and organic bonds. The three peaks at lower wavenumber (green shaded region) indicate the Raman scattering from inorganic crystalline part, as discussed above. Rest of the peaks in dotted box at higher wavenumber are from organic capping ligands. Our $\text{Cs}_2\text{NaBiCl}_6$ NCs are expected to have oleic acid and oleylamine as capping ligands. It is difficult to distinguish between oleic acid and oleylamine C-H and C=C bonds since they have similar chain length and structure. The only different are their functional groups like COO^- in oleate and NH_3^+ in oleyl ammonium as they might remain in protonated and deprotonated forms while capping the NCs by weak acid-base interaction with metal centers or halides. The organic capping ligand are present in NCs but are absence in

the bulk crystals. This difference might also contribute to the difference in phase transition behavior of bulk and NCs of $\text{Cs}_2\text{NaBiCl}_6$.

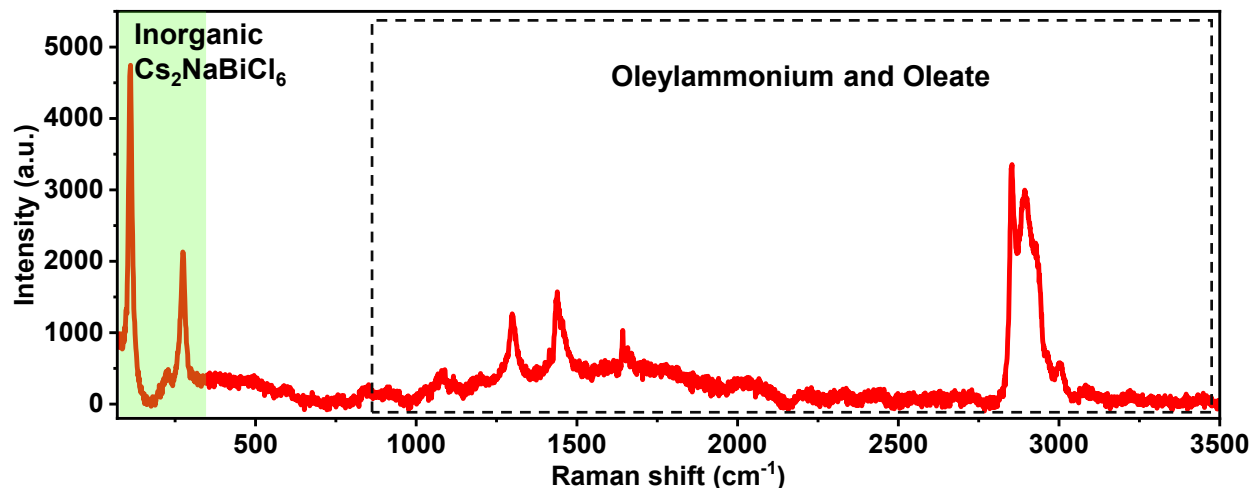


Figure 3.10: Raman spectrum of $\text{Cs}_2\text{NaBiCl}_6$ NCs film over an extended wavenumber range measured at room temperature.

3.3.3: Size Effect of Nanocrystals

We attribute the observed difference in structural phase transition property of bulk and nanocrystalline $\text{Cs}_2\text{NaBiCl}_6$ to the size. The surface to volume ratio increases sharply for nanocrystals. If we calculate the fraction in term of surface to volume ratio for a particle assuming it to be spherical, with radius r , total surface area is $4\pi r^2$ and volume is $\frac{4}{3}\pi r^3$, the ratio becomes,

$$\frac{\text{Surface area}}{\text{Volume}} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r} \quad (3.5)$$

Thus, the surface to volume ratio increases by 100 times by reducing the crystallite diameter from 1 μm (1000 nm) to 10 nm. In both bulk and nanocrystals of $\text{Cs}_2\text{NaBiCl}_6$, the surface terminates with the uncoordinated of metal centers (Na^+ , Bi^{3+}), A site cation (Cs^+) or halide (Cl^-). But the fraction of uncoordinated bonds on surface over coordinated ones in the core of the nanocrystal is significantly larger in case of nanocrystals because of the larger surface to volume ratio. Therefore, the different chemical compositions and atomic arrangements on the surface of nanocrystals contribute significantly more to the total energy of the nanocrystal, in comparison to

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the bulk counterpart. Consequently, the nanocrystals can have a different crystal structure at a given temperature compared to its bulk counterpart.

In addition to the simplistic enhancement of surface to volume ratio for nanocrystals, there are new chemical interaction of the organic capping ligands on the nanocrystal surface. In case of Cs₂NaBiCl₆ NCs, oleic acid and oleylamine have been used as capping ligands. The interaction of capping ligands will contribute to the total energy, which might also become important in inhibiting the cubic to tetragonal phase transition in Cs₂NaBiCl₆ NCs. Since we cannot here compare the different sizes of NCs with same capping ligands monitoring whether their phase transition property varies or not, thus the exact role of capping ligands on the phase transition property cannot be elucidated in a greater detail. But previously it has been observed, for similar size of crystal like CsPbI₃ removal of excess ligand stabilize cubic α -phase up to several days (~60 days) but excess of ligands help NCs convert to δ -phase after 2 days in air.⁶ A size dependent phase transition study for Cs₂NaBiCl₆ could have provided more insights on the critical size below which the phase transition stops, but the variable sized Cs₂NaBiCl₆ NCs was not obtained. Most of the reports on Cs₂NaBiCl₆ NCs even after changing the synthesis temperature reach up to size 10-20 nm only.^{17-19, 37}

3.4 Conclusions

In conclusion, bulk Cs₂NaBiCl₆ double perovskites undergo cubic to tetragonal phase transition below 110 K. But temperature dependent XRD and Raman spectroscopic study show that the colloidal Cs₂NaBiCl₆ nanocrystals (~12 nm size) do not show the phase transition. The nanocrystals retain the cubic phase in the entire temperature range of 300-10 K. We attribute this difference in phase transition properties of the bulk and nanocrystals to surface effect. Both (i) the large surface to volume ration, and (ii) the chemical interactions of organic capping ligands on the nanocrystal surface, are expected modify the total energy of the nanocrystal, suppressing the cubic to tetragonal phase transition. We note that the prior reports suggest most of the halide double perovskites show similar cubic to tetragonal phase transition at low temperatures, and therefore, our present study shows an interesting way to suppress this phase transition by employing the size-effect of nanocrystals.

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Chapter 4

High-Temperature Synthesis of Colloidal $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Perovskite Nanoplatelets and Nanocubes

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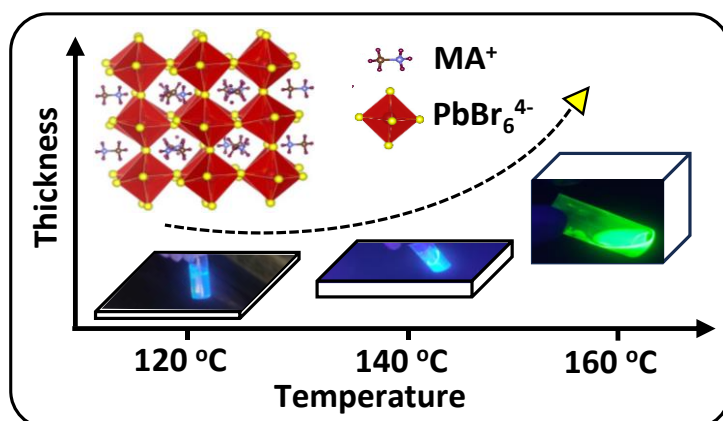
Chapter 4

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Abstract

Colloidal CsPbX_3 (X: Cl, Br, I) and FAPbX_3 (FA: formamidinium) perovskite nanocrystals (NCs) are well explored for their size-, shape- and surface-dependent optoelectronic properties. However, colloidal MAPbX_3 (MA: CH_3NH_3^+ , methyl ammonium) perovskite NCs are relatively less explored, though MAPbBr_3 nanoplatelets were the first halide perovskite NCs reported in literature. Often, the synthesis temperatures of MAPbBr_3 NCs are restricted to $\sim 65^\circ\text{C}$, keeping in mind the thermal instability of MA precursor solution. Here we advance the synthesis of MAPbBr_3 NCs in a non-polar medium by increasing the synthesis temperature in the range of $120^\circ\text{C} - 160^\circ\text{C}$. Colloidal MAPbBr_3 nanoplatelets with thicknesses 1.9 nm and 2.3 nm are prepared at 120°C and 140°C . It is to be noted that for the nanoplatelets, the molar ratio of $\text{MA}:\text{Pb} < 1$, along with a significant contribution from capping organic ligands. Further increase in the synthesis temperature to 160°C leads to the formation of MAPbBr_3 nanocubes with photoluminescence quantum yield 70-80%. The temperature-dependent control in size and shape of colloidal MAPbBr_3 NCs results into tuning the quantum confinement of excitons, yielding wavelength-tunable optical properties. This temperature-driven control of size and shape of MAPbBr_3 NCs, expand their potential for optoelectronic applications.

Graphical Abstract



4.1 Introduction

Organic–inorganic hybrid perovskite such as methylammonium lead halide has become one of the most promising materials for high-efficiency solar cells.¹⁻⁵ Also, such hybrid perovskites show high photoluminescence (PL) quantum yield making them potential candidates for applications light emitting diodes and lasing.⁶⁻⁸ Overall, the material class of hybrid halide perovskites are emerging as an interesting optoelectronic materials including futuristic applications such chiral optoelectronics and quantum light emitters.⁹⁻¹² These impressive optoelectronic properties of thin films and bulk samples of hybrid halide perovskites also motivated the synthesis of colloidal perovskite nanocrystals (NCs) exploring quantum-size effect and surface related phenomena.¹³ In this respect, a good progress has already been made for the colloidal all-inorganic CsPbX_3 NCs and FAPbX_3 (FA: formamidinium) NCs.¹⁴⁻²² But surprisingly, the scope of colloidal synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (MAPbBr_3 , MA: CH_3NH_3^+ or methylammonium) NCs remained limited, in spite of its first report in the year 2014 by Schmidt et al.²³ Here we advance the synthesis of colloidal MAPbBr_3 NCs in a non-polar medium, where nanoplatelets and nanocubes are synthesized by controlling the reaction temperatures.

Most of the prior reports of MAPbBr_3 NCs rely on a synthesis method known as ligand assisted reprecipitation (LARP).²³⁻²⁸ In this method, the synthesis is carried out near room temperature involving polar solvents like dimethylformamide (DMF) or dimethyl sulfoxide (DMSO). Zhang et al. improved the PL quantum yield of MAPbBr_3 NCs to ~70% with short chain ligands like n-octylamine in DMF but tuning the size and shape of NCs remained challenging.²⁴ In difference to LARP method, Vybornyi et al. reported the synthesis of MAPbBr_3 nanoplatelets in a non-polar medium 1-octadecene.²⁹ The nanoplatelets stacks to form nanowire like structure. In another synthesis using a non-polar medium, Imran et al. reported colloidal MAPbX_3 (X: Cl, Br, I) perovskite nanocubes using benzoyl halides as halide precursors.¹⁹ Quality of the obtained NCs were good maintaining both size-monodispersity and high PL quantum yield. The synthesis in non-polar medium appears to have a better control of NCs quality over LARP method.^{19, 30-32} However, for the synthesis in non-polar medium as well, the reaction temperature was restricted to ~65 °C, keeping in mind the low boiling point of methylamine solution in ethanol or other solvents.

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Here we increase the reaction temperatures of colloidal MAPbBr_3 NCs up to 160 °C, in a non-polar medium. The complex of methylamine and oleic acid, like MA-oleate ion-pair, appears to survive the high reaction temperature.³¹ The variation in synthesis temperature could yield different size and shape of NCs. Thin MAPbBr_3 nanoplatelets with thickness 1.9 nm were obtained at 120 °C, whereas thicker (2.3 nm thickness) nanoplatelets were obtained at 140 °C. Interestingly, increasing the reaction temperature to 160 °C yielded MAPbBr_3 nanocubes with edge-length ~14 nm. The control of size and shape in MAPbBr_3 NCs resulted into wavelength tunable excitonic optical absorption and emission properties. The nanocubes show an intense green emission with PL quantum yield in the range of 70-80%. The high temperature of 120 °C to 160 °C has not been explored earlier for the synthesis of MAPbBr_3 NCs, and therefore, our reports explore the potential of such synthesis enabling the temperature-dependent control of size and shape of MAPbBr_3 NCs.

4.2 Experimental Section

4.2.1 Chemicals

Lead (II) bromide (PbBr_2 , >98%, Sigma-Aldrich), oleic acid (90%, Sigma-Aldrich), oleylamine (>98%, Sigma-Aldrich), 1-octadecene (90%, Sigma-Aldrich), methylamine solution (33 wt% in absolute ethanol, Sigma-Aldrich), methyl acetate (99%, Sigma-Aldrich), hexane ($\geq 97\%$, Sigma-Aldrich).

4.2.2 Formation of A-site Methylammonium Cation

Upon formation of methylammonium oleate salt, carboxylic acid from oleic acid is expected to protonate methylamine thereby losing the carboxylic acid proton. Thus we expect a positive charge on nitrogen of methylammonium with chemical shift at higher δ value. For carboxylic acid we expect absence of the carboxylic acid hydrogen peak. We can see, in Figure 4.1a, NH_2 proton peak from methylamine in brown curve at 7 ppm, gets shifted to 7.8 ppm upon protonation in salt (pink curve). On the other hand the proton peak from carboxylic acid appearing at 11.7 ppm (in orange curve) is completely absent upon salt formation (pink curve). The missing of acidic proton from oleic acid to oleate complex is highlighted by yellow color in Figure 4.1a. Since ethanol doesn't take part in reaction, so no chemical shift is observed for the protons denoted by (c) and (d), they remain exactly in the same position in methylamine (brown curve)

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and methylammonium oleate (pink curve) in Figure 4.1b. Not only ethanol H, but the H next to COOH group upon deprotonation and hydrogen bond with NH_2 of methylamine shows upfield from 1.89 to 1.81 ppm also evidences salt formation.

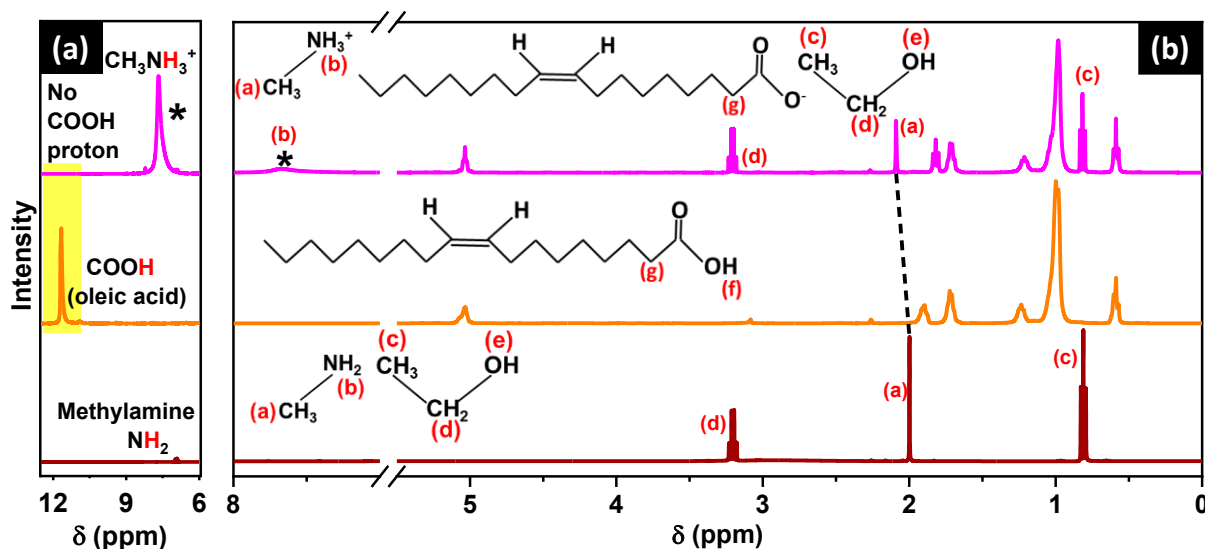


Figure 4.1: (a) y-axis Enlarged plot of ^1H NMR in the range of 6-12 ppm (b) lower full range ^1H NMR in the range of 0-8 ppm of Methylamine-Ethanol solution (bottom most brown curve), oleic acid (middle orange curve) and methylamine ethanol solution added in oleic acid (top most pink curve). In all cases dimethyl sulphoxide- d_6 (DMSO-d_6) is used as solvent for measurement purpose.

Figure 4.2 represents ^{13}C NMR of only methylamine, only oleic and oleic acid mixed with methylamine which is expected to give methylammonium oleate salt as also predicted ^1H NMR (Figure 4.1). The same samples are projected here to measure ^{13}C NMR, so the salt formation should reflect here also. Carbons from ethanol denoted by (b) and (c) do not show any chemical in methylamine ethanol solution (brown curve) and in methylammonium oleate (pink curve) since ethanol do not take part in any reaction. Rest components are only methylamine and oleic acid which form a salt and show shift in carbon that are up-fielded or down-fielded upon salt formation as compared to free acid and amine. For example, the carbon next to NH_2 group in methylamine, denoted by (a) has a chemical shift around 28.2 ppm shows a downfield in salt to 24.4 due to enhanced electron density over carbon. This is because the NH_3^+ group accepts electron density from COO^- via three H-bonds which were absent in free methylamine. For the same reason, electron density over carbon from carboxylic acid (COOH) in oleic acid is decreased in COO^- due to donation electron density to NH_3^+ via three H-bonds and experiences lack of electron density. Thus the carbon

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denoted by (d) in oleic acid has a lower value around 174 ppm (in orange curve) shifts to 176 ppm (in pink curve). Same effect is observed for the carbon next to COOH group denoted as (e) as expected. The carbons that are far away from carboxylic group like (f) are not affected by deprotonation, so they remain in same δ value.

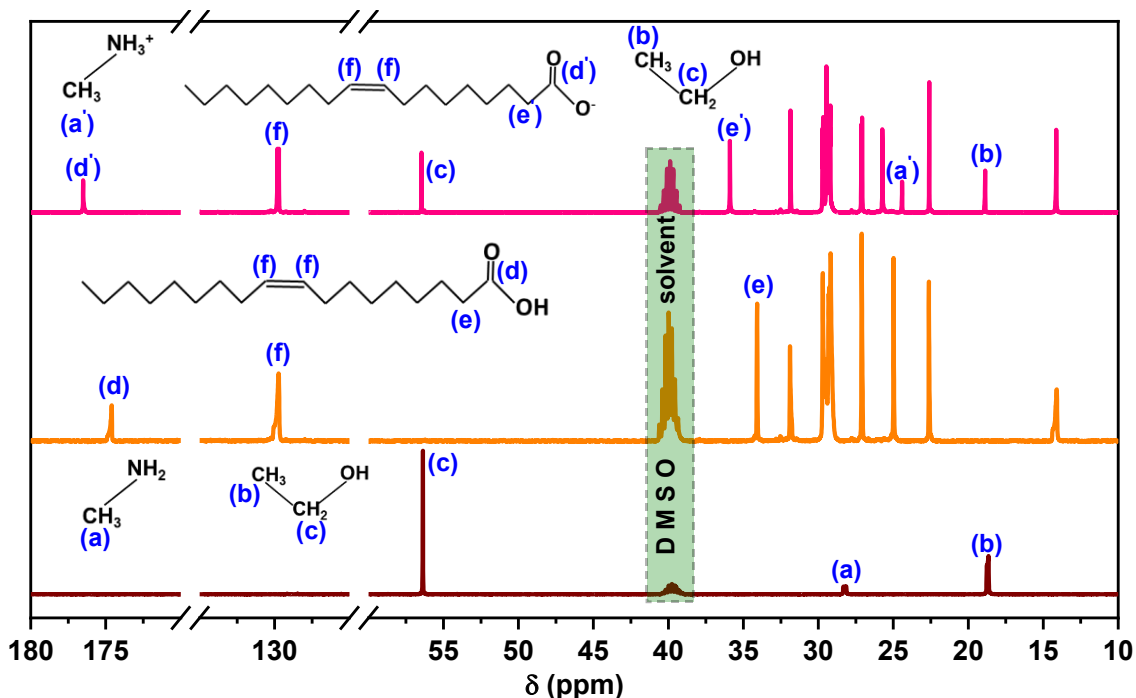


Figure 4.2: ^{13}C NMR (nuclear magnetic resonance) of methylamine in ethanol solution (bottom most brown curve), oleic acid (middle orange one), (methylamine ethanol solution added in oleic acid (top most pink curve). In all cases dimethyl sulphoxide- d_6 (DMSO-d_6) is used as solvent for measurement purpose.

4.2.3 Synthesis of MAPbBr_3 Nanocubes

Colloidal MAPbBr_3 NCs were synthesized in a non-polar medium using hot-injection method shown in Figure 4.3. 0.1 mmol (36.7 mg) PbBr_2 , 300 μl (0.95 mmol) oleic acid, 150 μl (0.45 mmol) oleylamine, and 5 ml 1-octadecene were taken in a 25 ml three-neck round bottom flask. The mixture was heated to 120 $^\circ\text{C}$ under N_2 flow by connecting to schlenk line yielding transparent yellow solution, and then kept under vacuum for 30 minutes at 120 $^\circ\text{C}$. Then the mixture was switched to N_2 atmosphere. In a separate micro centrifuge tube, 10 μl methylamine solution (33 wt% in ethanol) was mixed with 85 μl oleic acid (0.25 mmol) at room temperature. The oleic acid is expected to protonate the methylamine, thereafter, forming a complex like MA-oleate with reasonably good thermal stability.³¹ This mixture was then injected rapidly to the

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above PbBr_2 -oleic acid-oleylamine solution at 120 °C. The reaction mixture immediately turns off-white in color and becomes turbid. The reaction was allowed to proceed for 2 minutes, followed by quenching the reaction with ice-water bath. The reaction mixture at room temperature is then centrifuged at 7830 rpm for 5 minutes to precipitate out the NCs. Then the obtained NCs as precipitate were dispersed in 5 ml hexane and centrifuged for size selection at 5000 rpm for 3 minutes and transparent supernatant was collected. 2.5 ml methyl acetate was added dropwise to the supernatant until it becomes slightly turbid. Then the dispersion was centrifuged in 7830 rpm for 3 minutes for extracting the washed NCs as precipitate and re-dispersed in 3 ml hexane. This NC dispersion in hexane was stored for characterization and optical spectroscopy.

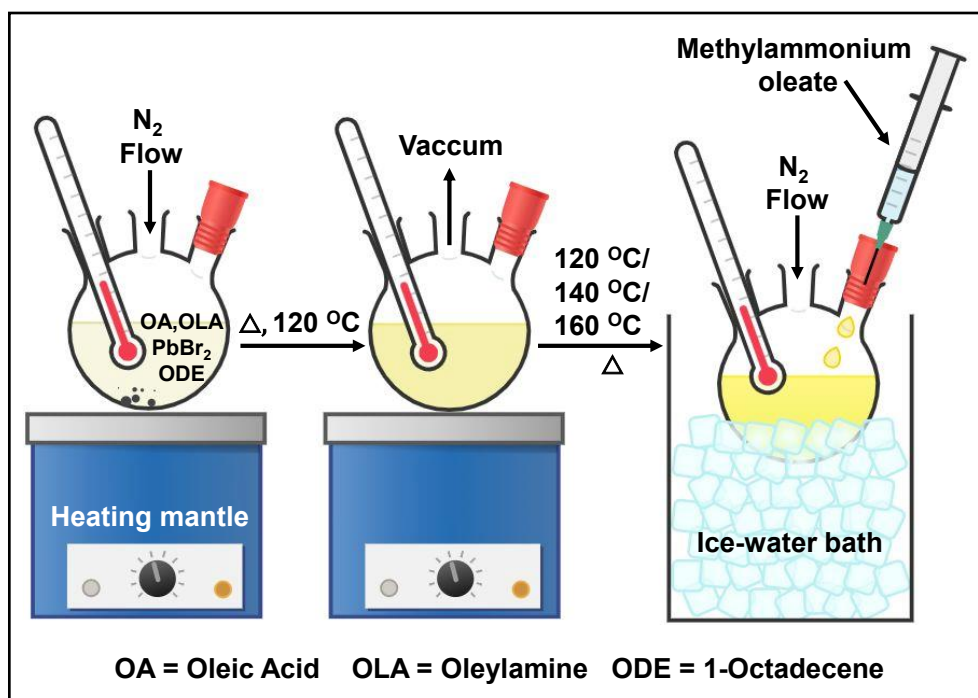


Figure 4.3: Reaction procedure for nanoplatelets at 120, 140 °C and nanocubes at 160 °C.

4.2.4 Synthesis of MAPbBr_3 Nanoplatelets at 120 °C and 140 °C

For carrying out the reactions at higher temperatures, 140 °C and 160 °C, the temperature of PbBr_2 -oleic acid-oleylamine precursor solution was raised to the respective temperatures under N_2 atmosphere, after vacuum treatment at 120 °C for 30 minutes. Subsequently, the methylamine-oleic acid mixture was injected at the respective temperature (140 °C or 160 °C). At 140 °C, the reaction was continued for

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90 seconds. At 160 °C, the reaction was continued for 10 seconds. The rest of the reaction and washing conditions were kept same as that for reaction carried out at 120 °C.

4.2.5 Characterization

All the optical absorption and emission data were collected using colloidal MAPbBr₃ NCs dispersed in hexane. UV-visible absorption spectra were recorded using a Perkin Elmer, Lambda-45 UV/Vis spectrometer. Steady state PL spectra were measured using Edinburgh FLS980 instrument. PL quantum yield of MAPbBr₃ NC dispersed in hexane was measured by using Rhodamine 6G (PL quantum yield 95%)³³ solution in ethanol as a reference dye. Powder X-ray diffraction (XRD) data were recorded using a Bruker D8 Advance x-ray diffractometer using Cu K α radiation (1.54 Å). The XRD samples for nanocrystals synthesized at 120 and 140 °C were prepared in two ways: one by spin-coating and another by drop-casting the colloidal NCs (in hexane) on glass substrate. The XRD sample NCs synthesized at 160 °C was prepared only by drop-casting the colloidal NCs on glass substrate. Transmission electron microscopy (TEM) experiments were carried out by using a JEOL JEM 2100F field emission transmission electron microscope at 200 kV. TEM samples were prepared by drop-casting very diluted NC dispersions in hexane on 200 mesh carbon coated copper grids, followed by drying under IR lamp (10-12 minutes), and then drying in vacuum for 12-14 hours.

4.3 Results and Discussion

4.3.1 MAPbBr₃ Nanoplatelets Synthesized at 120 °C and 140 °C

Colloidal synthesis of MAPbBr₃ NCs in non-polar medium gives two dimensional nanoplatelets with different thicknesses, when the reaction temperatures are 120 °C and 140 °C. TEM image of the NCs prepared at 120 °C is shown in Figure 4.4a. The image suggests the formation of thin nanoplatelets. Majority of the nanoplatelets are lying flat on the TEM grid, while some are lying perpendicular to the grid probably because of short-range self-assembly of the nanoplatelets. From those perpendicular nanoplatelets, an average thickness of nanoplatelets can be estimated to be around 1.9 nm, as shown by the size distribution plot in Figure 4.4b. The lateral shape of the nanoplatelets appears to be predominantly rectangular or square, but the poor

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contrast of thin nanoplatelets makes it difficult to estimate both length and breadth of the flat-lying nanoplatelets. Using the nanoplatelets lying perpendicular to the TEM image, the length (or breadth) the nanoplatelets is found to be 18.6 nm, as shown by the Figure 4.4c.

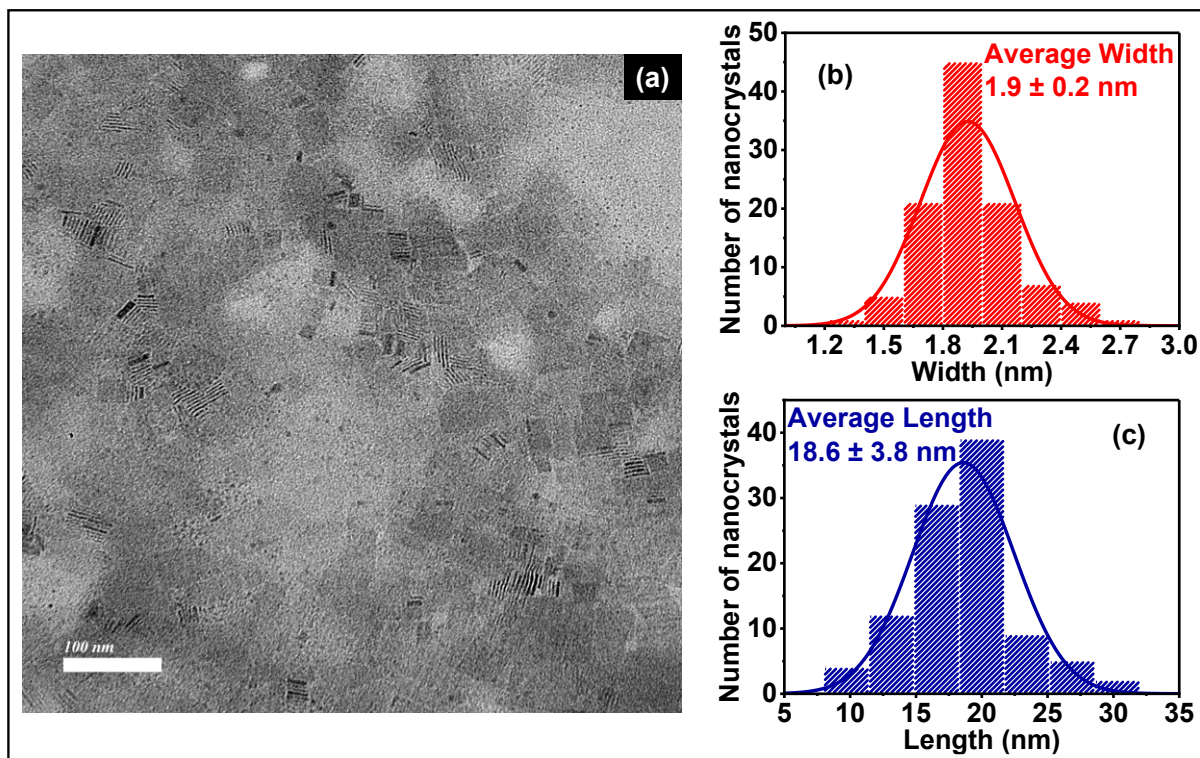


Figure 4.4: (a) TEM image of MAPbBr_3 nanoplatelets synthesized at 120 °C. Distribution of (b) thickness and (c) edge-length (or breadth) MAPbBr_3 nanoplatelets synthesized at 120 °C. The distribution is obtained from the corresponding TEM images of the sample.

To further verify the formation of MAPbBr_3 nanoplatelets, we show the UV-visible absorption and emission spectra in Figure 4.5. Sharp excitonic absorption features are observed, suggesting a strong quantum confinement of the electron-hole pair. Such quantum confinement is expected for a 1.9 nm thick MAPbBr_3 nanoplatelets, since the thickness is significantly smaller than the reported Bohr excitonic radius (4.4 nm).^{34, 35} The lowest energy excitonic absorption peak of the MAPbBr_3 nanoplatelets is at 443 nm (2.80 eV). This excitonic absorption energy is significantly higher than the reported bandgap (2.3 eV, 539 nm)^{35, 36} of bulk MAPbBr_3 , again corroborating the strong quantum confinement effect in our nanoplatelets. The nanoplatelets prepared at 120 °C also show a sharp excitonic emission with a peak at 452 nm (2.74 eV), with a small Stokes shift of 0.06 eV.

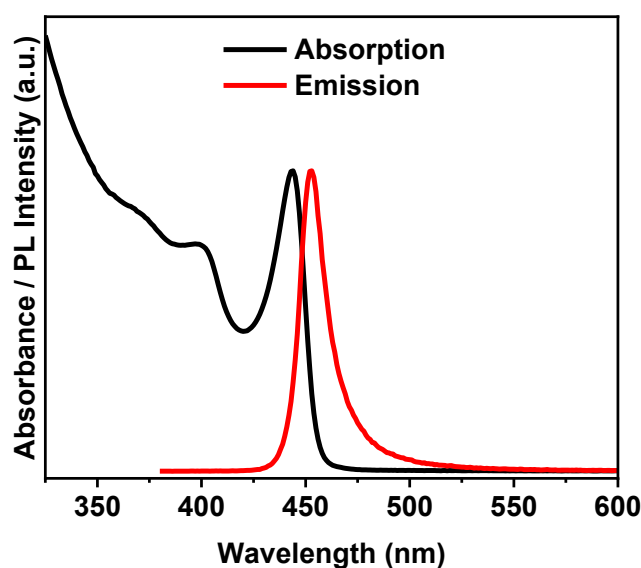


Figure 4.5: UV-visible absorption and PL emission of colloidal MAPbBr_3 nanoplatelets synthesized at 120 °C, PL emission spectra were collected after excitation at 365 nm.

Next, we discuss about the morphology and optical properties of the MAPbBr_3 NCs synthesized at 140 °C. TEM image in Figure 4.6a indicates formation of nanoplatelets at 140 °C as well. Again, some of the nanoplatelets are lying flat on the TEM grid, and some self-assembled nanocrystals are lying vertical on the grid. But compared to Figure 4.4a, the nanoplatelets in Figure 4.6a shows higher contrast, suggesting a higher thickness for nanoplatelets in Figure 4.4a. We estimate a thickness of around 2.3 nm and length (or breadth) around 14.2 nm from nanoplatelets that are stacked vertically on the grid. The size distribution plots are shown in Figure 4.6b,c. So, the TEM analysis suggests the formation of thicker nanoplatelets at 140 °C reaction temperature, compared to that at 120 °C.

To corroborate this fact, we also show the UV-visible absorption and emission spectra of the thicker nanoplatelets in Figure 4.7. Sharp excitonic absorption and emission are observed for 2.3 nm thick platelets, which are still significantly smaller than the Bohr excitonic diameter of MAPbBr_3 . However, the lowest energy excitonic absorption peak (464 nm, 2.67 eV) and the corresponding excitonic emission peak (472 nm, 2.63 eV) for the nanoplatelets prepared at 140 °C are significantly red-shifted compared to nanoplatelets prepared at 120 °C. This red-shift in absorption spectra agrees with the increased thickness in TEM image for nanoplatelets prepared at 140 °C.

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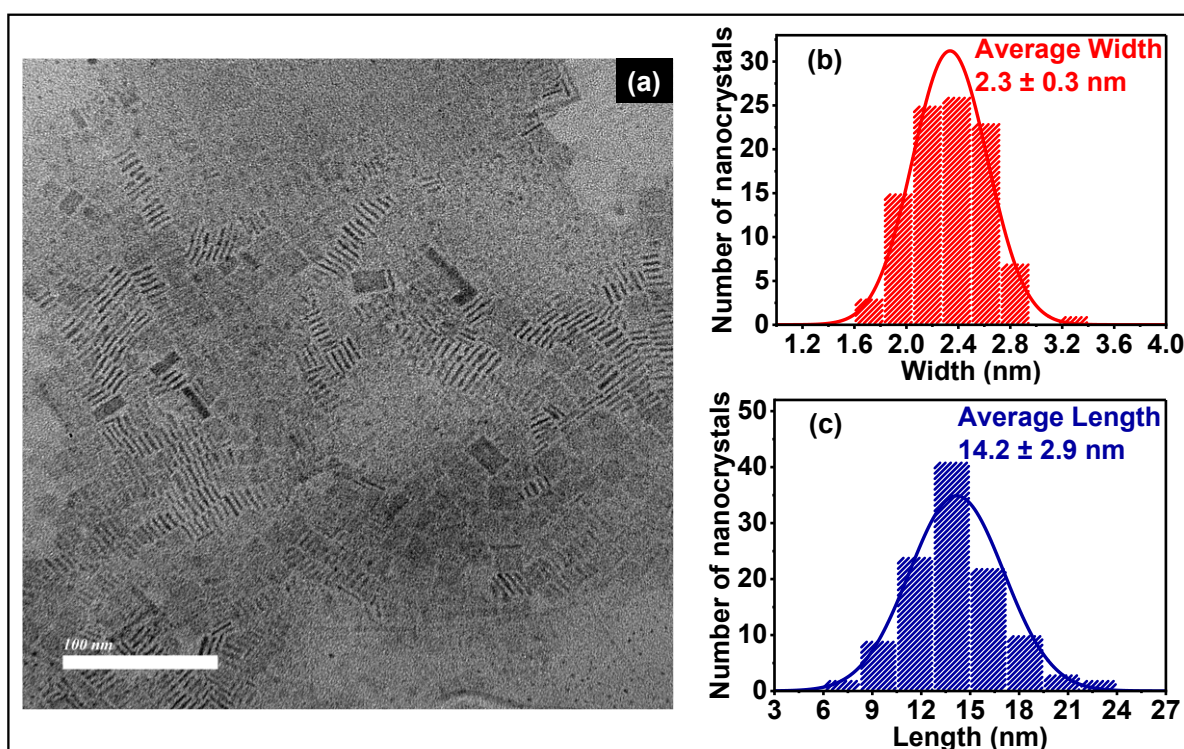


Figure 4.6: (a) TEM image of MAPbBr_3 nanoplatelets synthesized at 140 °C. Distribution of (b) thickness and (c) edge-length (or breadth) MAPbBr_3 nanoplatelets synthesized at 140 °C. The distribution is obtained from the corresponding TEM images of the sample.

To have more insights on the thickness-dependent quantum confinement, we compare our MAPbBr_3 nanoplatelets with that of layered pseudo two dimensional (2D) perovskites $\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{Br}_{3n+1}$, where PEA = phenylethyl ammonium and n is an integer. In this layered perovskite, $n = 1$ corresponds to a 2D $\text{PEA}_2\text{PbBr}_4$ with an excitonic absorption at ~ 395 nm (3.14 eV) and emission maxima at ~ 410 nm (3.01 eV).³⁷⁻⁴⁰ The thickness of the semiconducting Pb-Br monolayer is only ~ 0.59 nm, and therefore, the quantum confinement effect is stronger compared to our colloidal MAPbBr_3 nanoplatelets with thickness 1.9 nm. For $n = 2$ and 3, there are two and three connected Pb-Br layers in $\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{Br}_{3n+1}$, respectively. As n increases, the thickness of semiconducting Pb-Br layer (which also contain MA) increases. It has been reported that $n = 2$, and $n = 3$ show excitonic absorption peaks at 431 and 450 nm, respectively.³⁸ Therefore, the excitonic absorption peak of 443 nm for our MAPbBr_3 nanoplatelets prepared at 120 °C resembles with that of $n = 3$ of $\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{Br}_{3n+1}$. Also, three mono-layers of Pb-Br network ($\sim 3 \times 0.59$ nm) for $n =$

3 sample is similar to the 1.9 nm thickness of our MAPbBr_3 nanoplatelets (Figure 1a) synthesized at 120 °C.

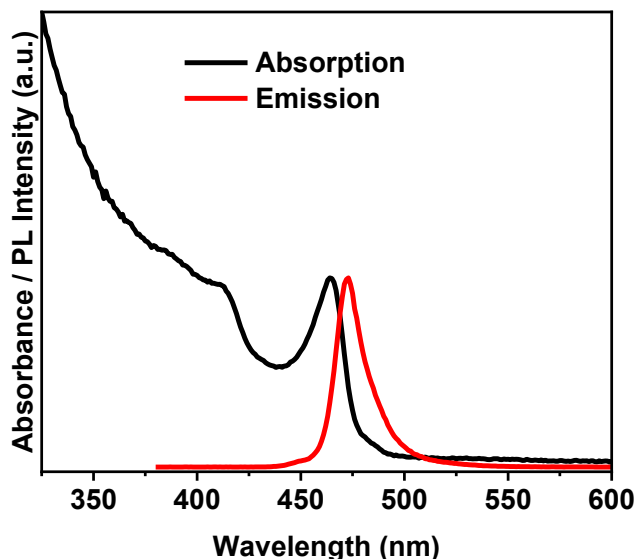


Figure 4.7: UV-visible absorption and PL emission of colloidal MAPbBr_3 nanoplatelets synthesized at 140 °C, PL emission spectra were collected after excitation at 365 nm.

In this analogy, MA:Pb molar ratio will be around 2:3 (similar to $n = 3$ layered hybrid perovskites) for our 1.9 nm thick nanoplatelets. But for the sake of simplicity, here we continue to name it as MAPbBr_3 nanoplatelets. Likewise, the excitonic absorption and emission energy of 2.3 nm thick MAPbBr_3 nanoplatelets (Figure 1c) prepared at 140 °C resembles with that of $n = 4$ samples of $\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{Br}_{3n+1}$.³⁸ For $n = 4$, the MA:Pb molar ratio is expected to be 3:4. It is noteworthy that the distributions of thicknesses in our MAPbBr_3 nanoplatelets are quite narrow (Figure 4.4b and 4.6b), which is also reflected in the single narrow emission peak (Figure 4.5 and 4.7) observed for the colloidal nanoplatelet samples. Obtaining such single emission peak is sometime difficult from the films and powder samples of $\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{Br}_{3n+1}$, because of contributions from different values of n within the same sample.

Figure 4.8a compares the powder XRD patterns of the nanoplatelets with that of reference data for cubic phase of bulk MAPbBr_3 . For XRD measurements, the same nanoplatelet sample (synthesized at 120 °C) were cast on glass slides in two different ways: by drop-casting and by spin-coating the colloidal NCs dispersed in hexane. The spin-coated nanoplatelets show major XRD peaks for (100) and (200) planes of cubic

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phase of MAPbBr_3 , along with a few other minor peaks of the same phase. This matching suggests the formation of cubic phase MAPbBr_3 nanoplatelets that were synthesized at 120 °C. But the nanoplatelets are oriented in a preferred stacking direction on the glass substrate enhancing the XRD intensities of (h00) planes.^{41, 42} TEM image in Figure 4.4a also suggested similar stacking of nanoplatelets. Such staking depends on the drying process of colloidal NCs on glass substrate. Slower evaporation of solvent is expected to yield more stacking. So, we drop-cast the same nanoplatelet sample (synthesized at 120 °C) on glass with slower evaporation of the solvent compared to the spin-coated film. Expectedly, the drop-cast sample also shows the dominance of (100) and (200) powder XRD peaks similar to the spin-coated one. Interestingly, the drop-cast sample show new peaks at lower 2θ values of 13.4° and 11.7°, for the nanoplatelets synthesized at 120 °C. Actually, a relook at the XRD pattern of the spin-coated sample also identifies the lower 2θ peaks at 13.7° and 11.9°, but with reduced intensities.

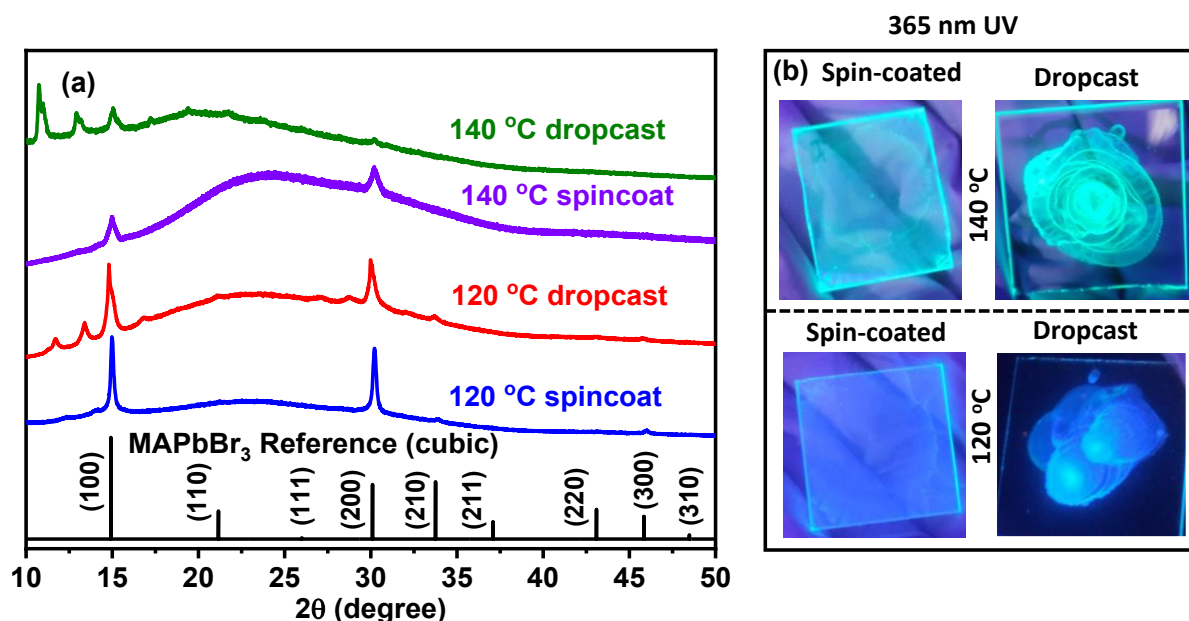


Figure 4.8: (a) Powder XRD patterns of MAPbBr_3 nanoplatelets synthesized at 120 °C and 140 °C. For XRD measurements, each of the samples were coated on glass slides by two methods, spin-coating and drop-casting. Reference XRD data for bulk MAPbBr_3 in cubic phase (CCDC#1446529) is also shown. (b) Photographs of spin-coated (left) and drop-cast (right) films (for which powder XRD measurements were carried out) under UV illumination.

In a cubic phase, the highest possible interplanar distance is for the (100) plane, which is at $2\theta = 14.9^\circ$. So, the lower 2θ peaks at 13.4° and 11.7° are not part of the

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cubic phase of MAPbBr_3 . Instead, these new peaks originate from the formation of self-assembled stacking of nanoplatelets. It has been reported earlier that the halide perovskite nanoplatelet easily stacks in an ordered fashion because of their anisotropic shape and strong face-to-face interactions, yielding periodic XRD peaks at low 2θ values.^{43, 44} The stacking is preferred for the slower drying process of the drop-cast films compared to the fast-drying of the spin-coated films. Also, thickness of the drop-cast films are supposed to be higher. Therefore, the lower 2θ peaks at 13.4° and 11.7° are more prominent for the drop-cast films (slow-drying and thicker films) compared to the spin-coated ones. At low angles, the XRD peaks are periodic with 2θ interval of 1.7° , corresponding to a stacking of the adjacent nanoplatelets synthesized at 120°C .

Powder XRD patterns of the nanoplatelets synthesized at 140°C (Figure 4.8a) also resembles with cubic phase of MAPbBr_3 , with dominance of (h00) peaks because of the preferred orientation of the nanoplatelets on the glass substrate. These nanoplatelets also show the repeating XRD peaks at 2θ values lower than that of (100) plane, similar to the nanoplatelets synthesized at 120°C . Expectedly, the lower 2θ peaks become more intense for the drop-cast sample, because of the enhanced stacking of the nanoplatelets compared to the spin-coated sample. Importantly, the lower 2θ range peaks for nanoplatelets prepared at 140°C appear at 12.9° and 10.7° , which are lower than that (13.4° and 11.7°) for nanoplatelets prepared at 120°C . This difference is perhaps expected, since thickness of nanoplatelets prepared at 140°C (2.3 nm) is higher than that (1.9 nm) prepared at 120°C .

Figure 4.8b shows the photographs of the spin-coated (thinner) and drop-cast (thicker) films of the sample under UV illuminations. Different hues of blue-green emissions are observed, corroborating the spectral data of their colloidal dispersion shown in Figure 4.5 and 4.7.

4.3.2 MAPbBr_3 Nanocubes Synthesized at 160°C

Interestingly, the characteristics of MAPbBr_3 NCs changed significantly, when the synthesis temperature was raised to 160°C . TEM image of the NCs in Figure 4.9a appears to exhibit cube morphology, or nanoplatelets with higher thickness. Vertical stacking, which is often observed in the case of nanoplatelets (see Figure 4.2a), is not

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observed in Figure 4.9a, suggesting that the NCs prepared at 160 °C are nanocubes, and not nanoplatelets. The average length of the cubes is around 14 ± 1.8 nm (Figure 4.9b), suggesting a good control over NC size and shape.

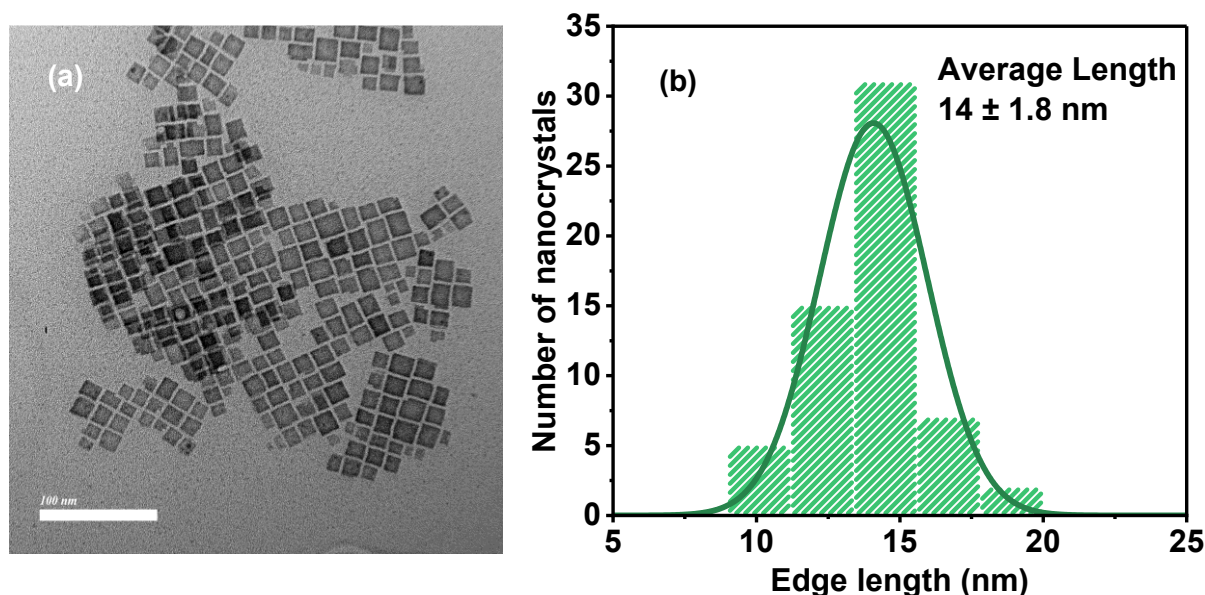


Figure 4.9: (a) TEM image (b) size distribution of MAPbBr_3 nanocubes synthesized at 160 °C.

High resolution TEM (HRTEM) image of a NC is shown in Figure 4.10. Lattice fringes are clearly observed. Interplanar distance of 2.6 Å in the HRTEM image can be assigned to (210) plane MAPbBr_3 in cubic phase. The edge-length (14 nm) of the nanocubes is significantly higher than the Bohr excitonic radius of MAPbBr_3 . So, in the lateral dimension, quantum confinement is weak or absent. The UV-visible absorption spectrum in Figure 4.11 does not show the sharp excitonic transitions, unlike Figure 4.5 and 4.7. The lowest energy optical absorption in Figure 4.11 is 519 nm (2.39 eV), which is closer to the band gap of bulk MAPbBr_3 . The NCs prepared at 160 °C does not show strong quantum confinement. Therefore, based on the TEM image in Figure 4.9a, and the absence of strong quantum confinement, we assign the NCs prepared at 160 °C as MAPbBr_3 nanocubes. The sample also show band edge excitonic emission with peak at 528 nm (2.35 eV). The freshly prepared sample shows a high relative PL quantum yield in the range of 70-80%, emphasising the good quality of the synthesized MAPbBr_3 nanocubes.

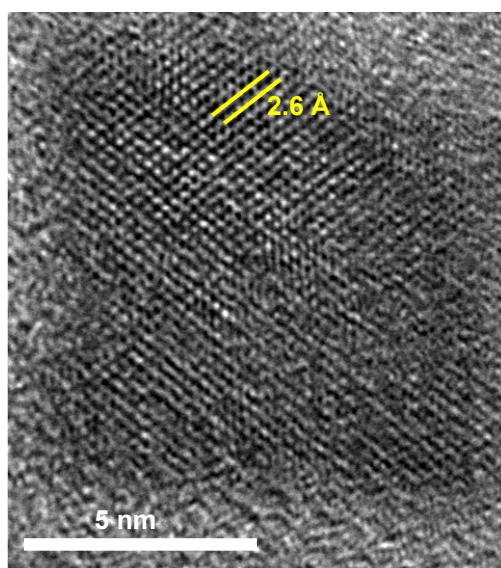


Figure 4.10: HRTEM image of a single MAPbBr₃ nanocube synthesized at 160 °C.

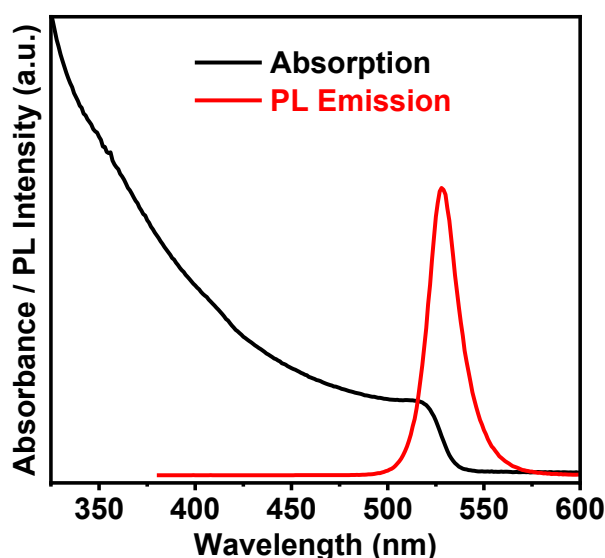


Figure 4.11: UV-visible absorption and PL emission of colloidal MAPbBr₃ nanocubes synthesized at 160 °C, PL emission spectra were collected after excitation at 365 nm.

In general, MAPbBr₃ forms a stable perovskite phase at room temperature.⁴⁵ But the colloidal stability of their nanocrystals is often challenging. For example, it has been reported that the MAPbBr₃ nanoplatelets have a tendency to stack with each other, and consequently, precipitates out of the dispersion after a certain time period.²⁹ Perhaps, we have also observed similar phenomenon where the freshly prepared MAPbBr₃ nanoplatelets forms clear colloidal dispersion allowing us to conduct spectroscopic measurements (Figure 4.5), but after 2 days, the nanoplatelets precipitate out. Compared to nanoplatelets, the MAPbBr₃ nanocubes show improved

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colloidal stability. This improvement is probably because of lesser stacking tendency of nanocubes. Figure 4.12a shows photograph of a clear colloidal dispersion of freshly prepared MAPbBr_3 nanocubes in hexane. The colloidal dispersion is retained till about 5 days of storage in the ambient conditions. But after that, the dispersion becomes turbid, as shown by the photograph in Figure 4.12b. However, the sample still show the green emission, ensuring its phase stability. It is noteworthy that the decrease in colloidal stability (or a turbid dispersion) of nanocrystals typically hampers the optical absorption and emission properties.

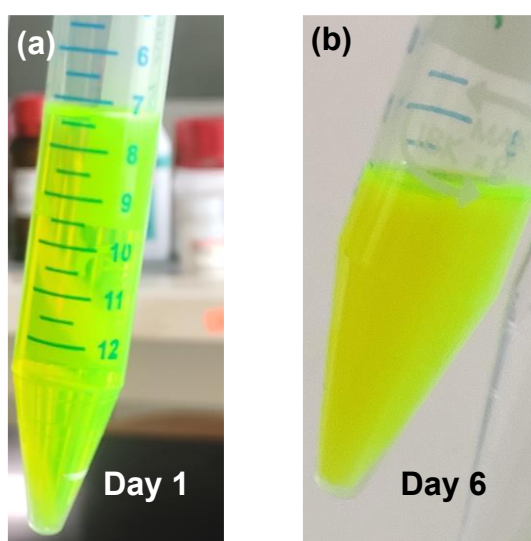


Figure 4.12: (a) Digital photograph of freshly prepared colloidal MAPbBr_3 nanocubes in hexane. The dispersion maintains colloidal stability for about 5 days of storage in ambient conditions, after which, it becomes turbid (b).

4.4 Conclusions

We have synthesized MAPbBr_3 NCs in a non-polar medium using hot-injection method. MAPbBr_3 nanoplatelets with thicknesses 1.9 nm and 2.3 nm are formed at a reaction temperature of 120 °C and 140 °C. The thicknesses of both the nanoplatelets are significantly smaller than the Bohr excitonic radius (4.4 nm)^{34, 35} of MAPbBr_3 . Consequently, strong quantum confinement effect is observed for both the nanoplatelets showing sharp excitonic absorption and emission in the blue spectral region. The spectra of the thicker platelets red-shift compared to the thinner ones owing to the smaller quantum confinement effect in the thicker nanoplatelets. Powder XRD patterns of both nanoplatelet samples suggest the formation of cubic phase of

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MAPbBr₃, along with peaks at lower 2θ values because of stacking of nanoplatelets on glass slides. When the reaction temperature was increased to 160 °C, colloidal MAPbBr₃ nanocubes with an average edge length of 14 nm are formed. These nanocubes show intense green PL emission with quantum yield 70-80%. Though the crystal phase of the MAPbBr₃ NCs are stable at room temperature, the colloidal stability of the nanoplatelets is limited to only 2 days because of their tendency to stack with each other and precipitate out. The nanocubes show a better colloidal stability for about 5 days, when stored in ambient conditions.

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Chapter 5

Thesis Summary and Future Outlook

5.1 Thesis Summary

Structural phase transition is very commonly observed in halide double perovskites as a function of external conditions like temperature, pressure. This crystal structure change can be probed by their changes in photophysical process like absorption, emission. $\text{Cs}_2\text{NaBiCl}_6$ is such an example which crystallizes in cubic ($Fm-3m$) crystal structure at room temperature but converts to tetragonal ($I4/mmm$) below 110 K. The crystal structure change influences the photophysical properties of the material. But to i) introduce luminescent centers in non-photo emissive $\text{Cs}_2\text{NaBiCl}_6$, ii) understand whether global structural changes alter local metal center's environment, iii) understand whether doping of foreign element alters phase transition behavior of the host or not, Mn^{2+} and Mo^{3+} have been doped and their emission behavior have been discussed in chapter 2A and 2B respectively. Mn^{2+} and Mo^{3+} are chosen because they both are *d*-block transition metals and show emission in octahedral coordination when doped in halide perovskites and *d-d* transition are usually sensitive to the surroundings.

Doping Mn^{2+} ions leads to a broad orange-red colored emission owing to its *d-d* electronic transition with broad FWHM around 184 meV at room temperature. It has been found that neither Mn^{2+} -doping alters the phase transition of the host around 110 K, nor the phase the transition alters the dopant emission. The emission depends on the local structure around the Mn^{2+} ions, which appears to remain unaffected, throughout the temperature range from 300 - 7K despite the global phase transition in the host (around ~ 100 K) (Figure 5.1), as also the Electron paramagnetic resonance for Mn^{2+} both in cubic and tetragonal environment of the host, suggest. In difference, the Mo^{3+} dopants show a sharp near-infrared emission (~ 1095 nm), known as intra-configurational spin-flipped transition that shows anomalous behavior around phase transition temperature (Figure 5.1). The probable reason for the discontinuous behavior of Mo^{3+} sharp emission is related to cubic to tetragonal distortion of local environment. Because the discontinuous behavior is absent in a system which does not undergo phase transition, like $\text{Cs}_2\text{NaInCl}_6$, when compared. But what happens to the emissive electronic states of Mo^{3+} is yet to be understood.

Furthermore, the structural phase transition behavior might change for nanocrystals, because of the higher contribution of the surface energy. The

uncoordinated or dangling bonds make the surface atoms different than the core ones. The fraction of surface atoms is much higher in nanocrystals than bulk, that makes significant difference in their total energy and feasibility to undergo a thermodynamically favorable process showing phase transition. Like bulk $\text{Cs}_2\text{NaBiCl}_6$ nanocrystals crystallizes in cubic structure at room temperature, indeed, our data do not show the signature of the cubic to tetragonal transition of $\text{Cs}_2\text{NaBiCl}_6$ nanocrystals ~ 110 K, unlike their bulk counterpart, as discussed in chapter 3 (Figure 5.1).

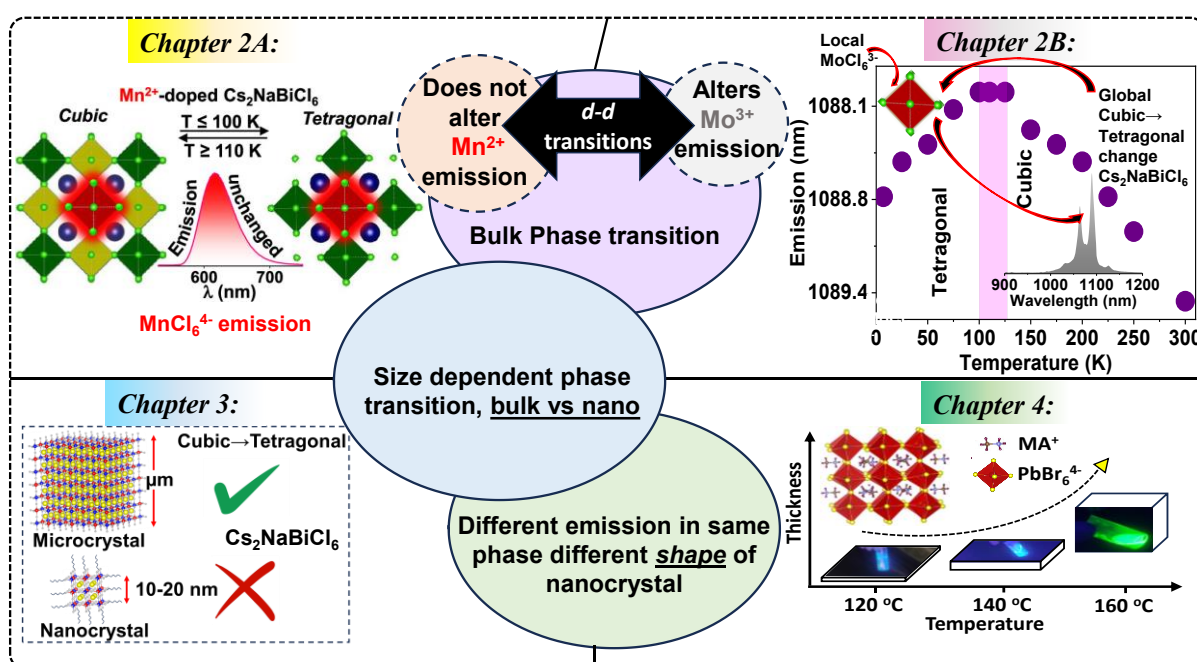


Figure 5.1: Graphical summary of the thesis. Effect of phase transition of $\text{Cs}_2\text{NaBiCl}_6$, on emission of transition metal-halide octahedral MnCl_6^{4-} and MoCl_6^{3-} under cubic and tetragonal crystal structure (chapter 2A and 2B), a size dependent phase transition study in $\text{Cs}_2\text{NaBiCl}_6$, nanocrystal not showing cubic to tetragonal phase transition unlike bulk counterpart (chapter 3). Shape dependent optical properties of colloidal MAPbBr_3 nanoplatelet and nanocubes showing strong quantum confinement driven emission color (chapter 4).

Lastly, we prepared colloidal methylammonium lead bromide (MAPbBr_3) nanocrystals with different shapes— nano cubes and nanoplatelets. The optical properties of MAPbBr_3 are hugely dependent on their shape and size showing strong quantum confinement effect. The nanoplatelets, along with their capping ligands, behave more like pseudo two-dimensional perovskites. The nanoplatelets have a tendency to stack among themselves but when the nanocrystal dispersion is spin

coated on substrate, while slow solvent evaporation allows them to stack in greater extent. These stacked nanoplatelets act as superlattices where the single nanoplatelets act as the repeating unit. In contrast, the nanotubes do not show such stacking tendency upon drop cast. Overall, the thesis work provides insights into the interplay between dopants, dimensionality, and phase stability of halide perovskites for optoelectronic applications as presented in Figure 5.1.

5.2 Future Outlook

Usually the phase transition in halide perovskites occurs due to i) deviation from the Goldschmidt tolerance factor range, lowering the stability, ii) octahedral tilting and rotation iii) translation or rotation of A site cation.¹⁻⁴ For example, CsPbI₃ is unstable for low tolerance factor than 1 (0.807), and octahedral tilting PbI₆⁴⁻ around Cs⁺.⁵ Changing Cs⁺ to FA⁺ does not significantly enhance the phase stability but suffers from same phase instability from semiconducting α to non-semiconducting δ phase at room temperature. MAPbI₃ suffers from poor thermal stability because of volatile methylammonium cation.⁶

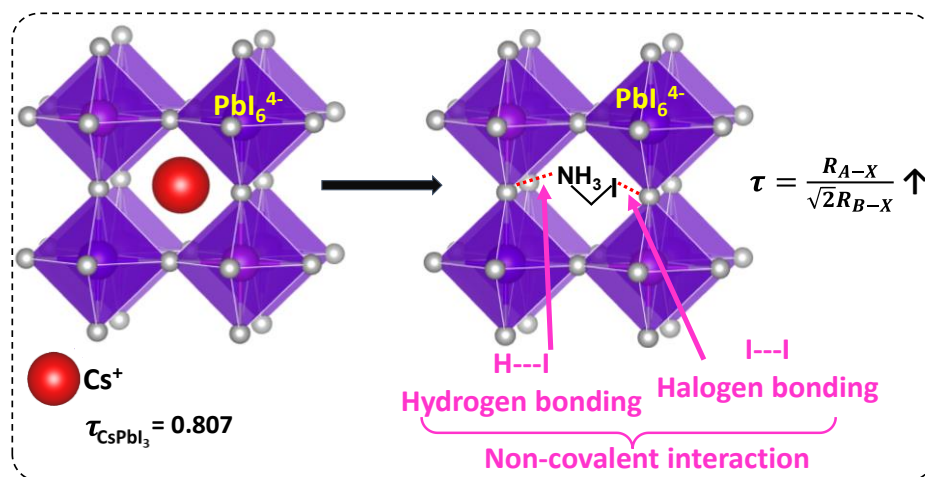


Figure 5.2: Schematic representation of CsPbI₃ perovskite, Cs⁺ replacement by bulky organic cation like (ICH₂NH₃)⁺, increasing the tolerance factor. Hydrogen bonding between iodine of PbI₆⁴⁻ octahedra and H of NH₃ head of A site cation (pink dotted line within the octahedral void) and halogen bonding between iodine of PbI₆⁴⁻ octahedra and iodine of A site cation (pink dotted line within the octahedral void) are introduced.

The replacement of Cs⁺ by a larger sized organic cation like I-CH₂-NH₃⁺ can increase the Goldschmidt tolerance factor. In presence of larger cation, the octahedral tilting can be arrested. Furthermore, the hydrogen bonding between iodine of PbI₆⁴⁻

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octahedra and H of NH₃ head of A site cation (shown with pink dotted line within the octahedral void in Figure 5.2) and halogen bonding between iodine of PbI₆⁴⁻ octahedra and iodine of A site cation (shown by pink dotted line within the octahedral void in Figure 5.2) can arrest the organic cation rotation and translation as well as octahedral tilting thereby introducing phase stability. By introducing two types of non-covalent interaction between A-site cation and halide of the octahedra may induce the phase stability to pb-I based three dimensional perovskite.

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Appendix A

Photoluminescence of $\text{Cs}_2\text{NaBiCl}_6$ at Cryogenic Temperature

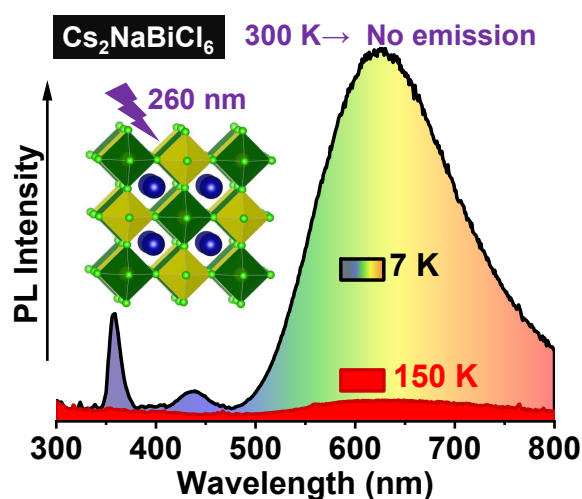
Appendix A

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Abstract

$\text{Cs}_2\text{NaBiCl}_6$, a double perovskite, has band edges mainly dominated by Bi^{3+} orbitals, which show a strong $ns^2 \rightarrow np^1$ absorption. Many of the earlier reports, Bi^{3+} is found to show emission when doped, but in spite of strong absorption, $\text{Cs}_2\text{NaBiCl}_6$ does not show any emission at room temperature. But when the temperature is lowered than ~ 50 K, a sharp emission starts to appear in UV region around 360 nm with an weak addition emission at 440 nm. The excitation spectra indicate the emission to appear from the Bi^{3+} centered transitions. Alongside, A broad self-trapped excitonic emission appears around 150 K, upon exciting the sample far above the band edges. All the emissions have a lifetime of micro- to milliseconds range indicating none of these are excitonic in nature. Most importantly, $\text{Cs}_2\text{NaBiCl}_6$ is well known to undergo a cubic to tetragonal phase transition below 110 K. Since the appearance of the emission are at temperatures far below (50 K) and above (150 K), these are not appearing because of the structural phase transition.

Graphical Abstract



Appendix A

Photoluminescence of $\text{Cs}_2\text{NaBiCl}_6$ at Cryogenic Temperature

A.1 Introduction

Halide double perovskites, have different electronic band structures from conventional lead or tin-based halide perovskites. The difference mainly appears due to the involvement of two different metal centers (monovalent and trivalent), substituting two bivalent metal centers.¹ On top of that, Na-based double perovskites such as $\text{Cs}_2\text{NaInCl}_6$ or $\text{Cs}_2\text{NaBiCl}_6$, band edges are dominated by In^{3+} or Bi^{3+} orbitals overlapping with halides (Cl^- here).² Because Na^+ valence orbitals lie much deeper inside the conduction or valence band. Now, In^{3+} having a parity forbidden transition, does not show intense absorption coming from In^{3+} center, on the other hand, Bi^{3+} , being as ns^2 ion, shows strong $ns^2 \rightarrow ns^1np^1$.³⁻⁶ Though the transition is spin-forbidden in nature, Jahn-Teller distortion around Bi^{3+} centers make the transition partially allowed ones. The distortion is like z-axis elongation or compression. In $\text{Cs}_2\text{NaBiCl}_6$, the peaks corresponding to Jahn Teller distortion allowed $ns^2 \rightarrow ns^1np^1$ transition, appear around 316 nm and 340 nm at room temperature as shown in Figure A.1.^{4, 5}

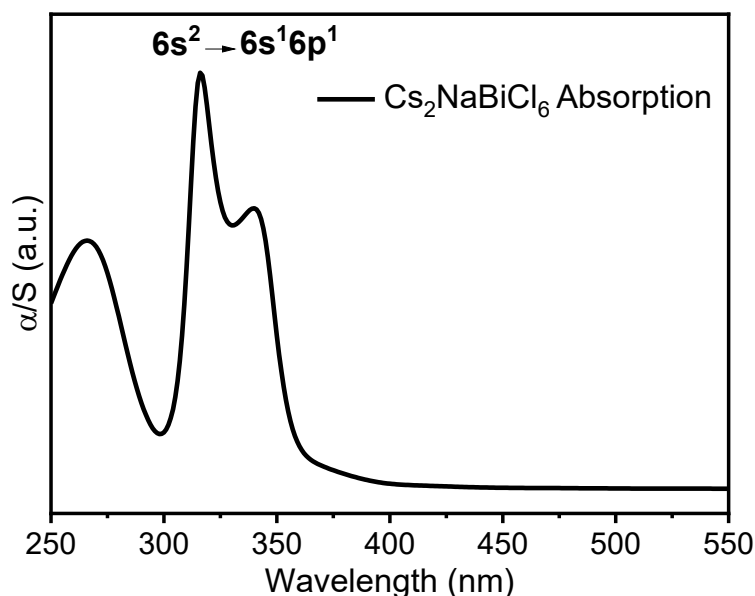


Figure A.1: Kubelka-Munk transformed absorption spectra of $\text{Cs}_2\text{NaBiCl}_6$ bulk.

Bi^{3+} emits due to de-excitation of same transition, only when doped in lower concentration in other hosts like Cs_2SnCl_6 , $\text{Cs}_2\text{AgInCl}_6$, $\text{Cs}_2\text{NaInCl}_6$.^{7, 8} Interestingly, when Bi^{3+} itself form a host, for example, no emission comes from Bi^{3+} centers although the band edges have mostly contribution from Bi^{3+} s and p orbitals. Thus,

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Photoluminescence of $\text{Cs}_2\text{NaBiCl}_6$ at Cryogenic Temperature

$\text{Cs}_2\text{NaBiCl}_6$ does not give any luminescence at room temperature. But when the temperature is lowered than 175 K, upon exciting the sample with 260 nm a broad emission peak centered at 627 nm is observed. Furthermore, when the temperature is even lowered than 50 K, upon exciting the sample with 315 nm gives sharp emission centered at 360 nm.

A.2 Experimental Section

The synthesis and characterization of $\text{Cs}_2\text{NaBiCl}_6$ crystals are the same as discussed in chapter 2A.

A.3 Results and Discussion

A.3.1 Temperature dependent photoluminescence $\text{Cs}_2\text{NaBiCl}_6$

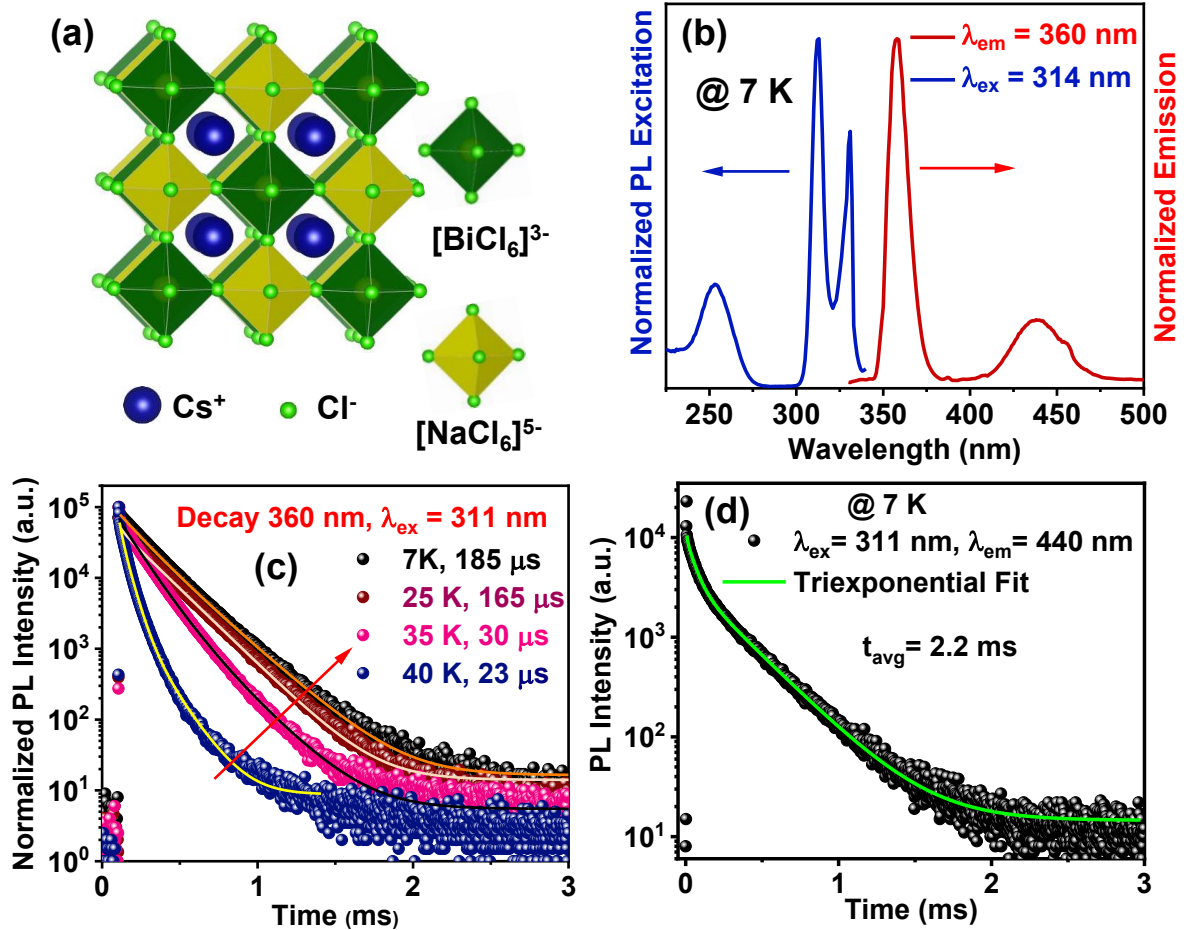


Figure A.2: (a) Schematic of $\text{Cs}_2\text{NaBiCl}_6$ at room temperature. (b) Emission spectra at $\lambda_{\text{ex}}=312$ nm and excitation spectra $\lambda_{\text{em}}= 360$ nm for undoped $\text{Cs}_2\text{NaBiCl}_6$ at 7 K. (c) Fitted lifetimes measured at $\lambda_{\text{ex}}=311$ nm and $\lambda_{\text{em}}= 360$ nm from 40-7 K. (d) Fitted Lifetime measured at $\lambda_{\text{ex}}=311$ nm and $\lambda_{\text{em}}= 440$ nm from 7 K.

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Photoluminescence of Cs₂NaBiCl₆ at Cryogenic Temperature

According to the PL excitation spectra in chapter 2A, Figure 2A.15, the sample can be excited at 315 nm, even for undoped Cs₂NaBiCl₆. Because this absorption corresponds to Bi³⁺ absorption. At room temperature exciting the sample at 315 nm, does not give any emission but below 50 K, the same excitation gives a sharp emission at 360 nm as shown in Figure A.2b. Figure A.2a shows the Schematic of undoped Cs₂NaBiCl₆ at room temperature. Upon exciting undoped Cs₂NaBiCl₆ with 312 nm, the 360 nm emission appears with an additional emission peak at 440 nm of low intensity. These peaks start appearing around 45 K and retains up to lowest possible temperature reached, 7 K. The two intense peaks appearing in PL excitation around 312 and 333 nm in Figure A.2b resembles with the Bi³⁺ Jahn-Teller distortion related peak evaluated with decrease in temperature. The emission peak at 360 nm has a lifetime in an order of hundreds of microseconds (Figure A.4c). The emission as 430 nm has a lifetime of 2.2 ms (Figure A.4d). The long lifetimes suggest that the sharp emissions are not definitely the excitonic one. Though the similar emission from Bismuth based complexes have been observed earlier, it can be said that the origin of these two emissions is probably from the Bi³⁺ centers but why they start appearing below 50 K is still unclear.

At 150 K, upon irradiation with 260 nm wavelength Cs₂NaBiCl₆ shows another broad emission mainly centered at ~627 nm (red region) (Figure A.3a). 260 nm is even higher in energy than the band edges, which not only is contributed from the s and p orbitals of Bi³⁺. This broad. emission in most of the cases is termed as self-trapped excitonic (STE) emission.⁹ This emission starting from 150 K, intensifies up to 7 K. The PL excitation spectra (blue curve in Figure A.3b) show that, the origin of the emission is not mainly the Bi³⁺ based transition but at even higher energy states around 260 nm (gray shaded part of the PL excitation spectra in Figure A.5b). The lifetime is found to be around 15 μ s (Figure A.3c). The digital image shows the red emission coming out of undoped Cs₂NaBiCl₆ upon 260 nm excitation below 125 K (Figure A.3d).

Since, Cs₂NaBiCl₆ is known to undergo a phase transition around 100 K, from cubic to tetragonal, it can be expected the features coming out of the structural change in Cs₂NaBiCl₆. But surprisingly, the emission peaks at 360 and 440 nm appears below 50 K. Also, the broad emission, STE, comes below 150 K. Meaning, appearance of

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Photoluminescence of $\text{Cs}_2\text{NaBiCl}_6$ at Cryogenic Temperature

these two peaks do not correspond to the phase transition property. The reason of sharp emission from Bi^{3+} centers below 50 K is yet to be understood.

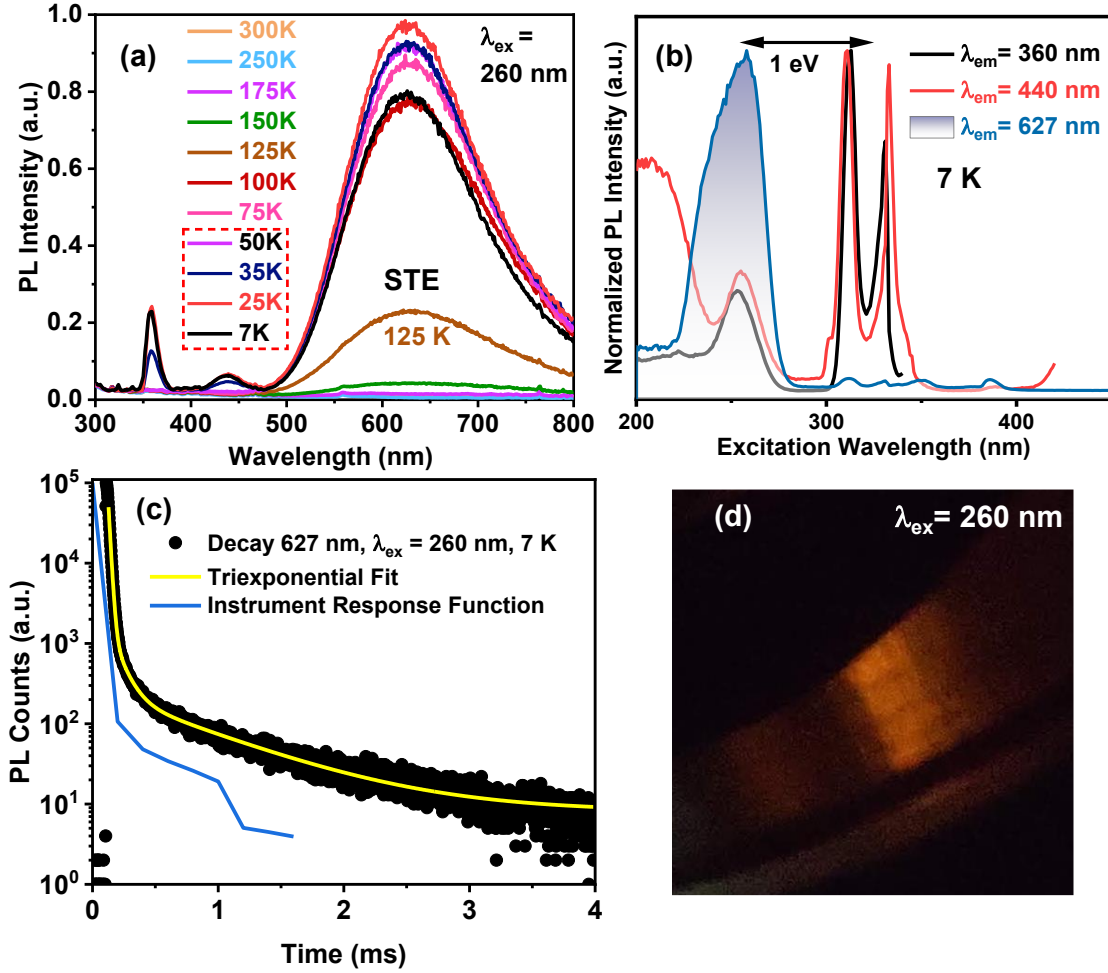


Figure A.3: (a) Emission spectra of Undoped $\text{Cs}_2\text{NaBiCl}_6$ with $\lambda_{\text{ex}} = 260$ nm from 300-7 K. (b) PL excitation peak for $\lambda_{\text{em}} = 360, 440$ and 627 nm. (c) Lifetime measured at $\lambda_{\text{ex}} = 260$ nm and $\lambda_{\text{em}} = 627$ nm at 7 K. (d) Digital image of red emission coming from the sample inside cryostat holder with 260 nm excitation below 125 K for undoped $\text{Cs}_2\text{NaBiCl}_6$.

A.4 Conclusions

Undoped $\text{Cs}_2\text{NaBiCl}_6$ does not emit light at room temperature. It undergoes a phase transition from cubic to tetragonal below 110 K. But it emits sharply at deep UV region at a temperature below 50 K. The excitation spectra resemble with the absorption of Bi^{3+} evolved at lower temperature with a microsecond lifetime. This suggests that the emission is not excitonic in nature and can be a result of Bi^{3+} partially forbidden transition. But still a sudden appearance of such emission is yet to be

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Photoluminescence of $\text{Cs}_2\text{NaBiCl}_6$ at Cryogenic Temperature

understood. Additionally, from 150 K-7 K, a broad red emission starts to come which resembles with the self-trapped excitonic emission. But all the emissions are clearly not coming due to the structural phase transition property since the transition temperature is far different (~ 100 K) from the temperatures, where the emissions start to appear.

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List of Publications

Included in the Thesis:

- ✚ **Banerjee, S.;** Saikia, S.; Molokeev, M. S.; Nag, A. Unveiling Temperature-Induced Structural Phase Transition and Luminescence in Mn²⁺-doped Cs₂NaBiCl₆ Double Perovskite. *Chem. Mater.* **2024**, 36, 4750-4757.
- ✚ **Banerjee, S.;** Nag, A. High-Temperature Synthesis of Colloidal CH₃NH₃PbBr₃ Perovskite Nanoplatelets and Nanocubes. *Energy Fuels* **2025**, 39, 11339–11345.
- ✚ **Banerjee, S.;** Joshi, A.; Saha, S.; Nag, A. Temperature Dependent Phase Transition in Cs₂NaBiCl₆ Nanocrystals:Size Effect (manuscript under preperation)

Not Included in the Thesis:

- ✚ Kshirsagar, A. S.; Arfin, H.; **Banerjee, S.;** Mondal, B.; Nag, A. Colloidal Sb³⁺-Doped Cs₂InCl₅·H₂O Perovskite Nanocrystals with Temperature-Dependent Luminescence. *J. Phys. Chem. C* **2021**, 125 (50), 27671-27677.
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		Volume	5
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2) **Description of Service.** CCC's Marketplace enables Users to obtain Licenses to use one or more Works in accordance with all relevant Terms. CCC grants Licenses as an agent on behalf of the copyright rightsholder identified in the relevant Order Confirmation.

3) **Applicability of Terms.** The Terms govern User's use of Works in connection with the relevant License. In the event of any conflict between General Terms and Order Confirmation Terms, the latter shall govern. User acknowledges that Rightsholders have complete discretion whether to grant any permission, and whether to place any limitations on any grant, and that CCC has no right to supersede or to modify any such discretionary act by a Rightsholder.

4) **Representations; Acceptance.** By using the Service, User represents and warrants that User has been duly authorized by the User to accept, and hereby does accept, all Terms.

5) **Scope of License; Limitations and Obligations.** All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The License provides only those rights expressly set forth in the terms and conveys no other rights in any Works

6) **General Payment Terms.** User may pay at time of checkout by credit card or choose to be invoiced. If the User chooses to be invoiced, the User shall: (i) remit payments in the manner identified on specific invoices, (ii) unless otherwise specifically stated in an Order Confirmation or separate written agreement, Users shall remit payments upon receipt of the relevant invoice from CCC, either by delivery or notification of availability of the invoice via the Marketplace platform, and (iii) if the User does not pay the invoice within 30 days of receipt, the User may incur a service charge of 1.5% per month or the maximum rate allowed by applicable law, whichever is less. While User may exercise the rights in the License immediately upon receiving the Order Confirmation, the License is automatically revoked and is null and void, as if it had never been issued, if CCC does not receive complete payment on a timely basis.

7) **General Limits on Use.** Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) involves only the rights set forth in the Terms and does not include subsequent or additional uses, (ii) is non-exclusive and non-transferable, and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Terms. Upon completion of the licensed use as set forth in the Order Confirmation, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work. User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is unlawful, including without limitation if such use would violate applicable sanctions laws or regulations, would be defamatory, violate the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit, or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. Any unlawful use will render any licenses hereunder null and void. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

8) **Third Party Materials.** In the event that the material for which a License is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) that are identified in such material as having been used by permission (or a similar indicator), User is responsible for identifying, and seeking separate licenses (under this Service, if available, or otherwise) for any of such third party materials; without a separate license, User may not use such third party materials via the License.

9) **Copyright Notice.** Use of proper copyright notice for a Work is required as a condition of any License granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Used with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc." Such notice must be provided in a reasonably legible font size and must be placed either on a cover page or in another location that any person, upon gaining access to the material which is the subject of a permission, shall see, or in the case of republication Licenses, immediately adjacent to the Work as used (for example, as part of a by-line or footnote) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

10) **Indemnity.** User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs, and expenses, including legal fees and expenses, arising out of

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14) Additional Terms for Specific Products and Services. If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) *Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).* For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) Books and Records; Right to Audit. As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

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i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content**, which grants authorizations to import requested material in electronic format, and allows electronic access to this material to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) **Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text**, which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

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ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii)

permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

F) User must ensure (through use of an electronic cover page or other appropriate means) that any person, upon gaining electronic access to the material, which is the subject of a permission, shall see:

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- a statement to the effect that such copy was made pursuant to permission,
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v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

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- ii) User may not make or permit any alterations to the Work, unless expressly set forth in the Order Confirmation (after request by User and approval by Rightsholder); provided, however, that a Work consisting of photographs or other still images not embedded in text may, if necessary, be resized, reformatted or have its resolution modified without additional express permission, and a Work consisting of audiovisual content may, if necessary, be “clipped” or reformatted for purposes of time or content management or ease of delivery (provided that any such resizing, reformatting, resolution modification or “clipping” does not alter the underlying editorial content or meaning of the Work used, and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular License described in the Order Confirmation and the Terms.

15) Miscellaneous.

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC’s privacy policy, available online at www.copyright.com/about/privacy-policy/.

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d) No amendment or waiver of any Terms is binding unless set forth in writing and signed by the appropriate parties, including, where applicable, the Rightsholder. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by or on behalf of the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the License described in the Order Confirmation, which terms are in any way inconsistent with any Terms set forth in the Order Confirmation, and/or in CCC’s standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

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Last updated October 2022



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Multifunctional Perovskite Photodetectors: From Molecular-Scale Crystal Structure Design to Micro/Nano-scale Morphology Manipulation**SPRINGER NATURE****Author:** Yingjie Zhao et al**Publication:** Nano-Micro Letters**Publisher:** Springer Nature**Date:** Jul 29, 2023*Copyright © 2023, The Author(s)***Creative Commons**

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Order Date	13-Nov-2025	Type of Use	Republish in a
Order License ID	1671574-1		thesis/dissertation
ISSN	2050-7496	Publisher Portion	Royal Society of Chemistry Image/photo/illustration

LICENSED CONTENT

Publication Title	Journal of materials chemistry. A, Materials for energy and sustainability	Publication Type	e-Journal
		Start Page	11124
		End Page	11144
Article Title	Stability of CsPbI ₃ perovskite: from Fundamentals to Improvements	Issue	18
		Volume	9
		URL	http://pubs.rsc.org/en/journals/journalissues/ta
Author / Editor	Royal Society of Chemistry (Great Britain)		
Date	01/01/2013		
Language	English		
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NEW WORK DETAILS

Title	Phase Transition, Doping (Mn ²⁺ and Mo ³⁺) and Luminescence of Cs ₂ NaBiCl ₆ and CH ₃ NH ₃ PbBr ₃ Perovskites: Bulk and Nanocrystals	Institution Name	IISER Pune
		Expected Presentation Date	2025-11-25
Instructor Name	Srijita Banerjee		

ADDITIONAL DETAILS

Order Reference Number	N/A	The Requesting Person / Organization to Appear on the License	Srijita Banerjee
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REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Figure 1	Title of the Article / Chapter the Portion Is From	Stability of CsPbI ₃ perovskite: from Fundamentals to Improvements
Editor of Portion(s)	Yao, Zhun; Zhao, Wangen; Liu, Shengzhong Frank	Author of Portion(s)	Yao, Zhun; Zhao, Wangen; Liu, Shengzhong Frank
Volume / Edition	9		
Page or Page Range of Portion	11124-11144	Issue, if Republishing an Article From a Serial	18
		Publication Date of Portion	2021-01-01

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2) **Description of Service.** CCC's Marketplace enables Users to obtain Licenses to use one or more Works in accordance with all relevant Terms. CCC grants Licenses as an agent on behalf of the copyright rightsholder identified in the relevant Order Confirmation.

3) **Applicability of Terms.** The Terms govern User's use of Works in connection with the relevant License. In the event of any conflict between General Terms and Order Confirmation Terms, the latter shall govern. User acknowledges that Rightsholders have complete discretion whether to grant any permission, and whether to place any limitations on any grant, and that CCC has no right to supersede or to modify any such discretionary act by a Rightsholder.

4) **Representations; Acceptance.** By using the Service, User represents and warrants that User has been duly authorized by the User to accept, and hereby does accept, all Terms.

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Last updated October 2022

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Article Title	Postsynthesis Mn-doping in CsPbI ₃ nanocrystals to stabilize the black perovskite phase.	Start Page	4278
		End Page	4286
		Issue	10
Author / Editor	Royal Society of Chemistry (Great Britain), National Center for Nanoscience and Technology.	Volume	11
		URL	http://www.rsc.org/Publishing/Journals/NR/index.asp
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Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Feb 1, 2017

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