

# Investigating a new pathway for the generation of Mn doped CsPbCl<sub>3</sub> perovskite nanocrystals

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*A dissertation submitted for the partial fulfilment of  
BS-MS dual degree in Science*



**Indian Institute of Science Education and Research Mohali**  
**April 2019**

## **Certificate of Examination**

This is to certify that the dissertation titled **Investigating a new pathway for the generation of Mn doped CsPbCl<sub>3</sub> perovskite nanocrystals** submitted by **Ms. Isabella Antony K.J (Reg.No.MS14105)** for the partial fulfillment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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## **Declaration**

The work presented in this dissertation has been carried out by me under the guidance of Dr. Debrina Jana at the Indian Institute of Science Education and Research Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Isabella Antony K.J  
(Candidate)

Dated: April 26, 2019

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Debrina Jana  
(Supervisor)

## **Acknowledgement**

I am really lucky and proud to have Dr. Debrina Jana as my supervisor. She is always a source of motivation. Her constant love, support and guidance keeps me motivated and energized to do my work. Her way of teaching on how to understand a problem and a systematic way of approaching it was extraordinary. The discussions we had and the innovative ideas produced from it will always remain as a great lesson for the success in my science career.

I gratefully acknowledge INSPIRE Faculty research grant (DST/INSPIRE/04/2015/002741), DST for funding this research work.

I would like to express thanks to my project committee members Dr. Ujjal K Gautam and Dr. Sanchita Sengupta for their time and many valuable suggestions that improved me to think more scientifically and understand the basic phenomena.

I would also like to thank IISER Mohali for providing me the adequate facilities and Department of Science and Technology, India for providing INSPIRE scholarship throughout my academic program. I am thankful to Prof. Sanjay Mandal for helping us characterizing samples in XRD (central research facility, IISER Mohali). I also thank Metrohm for helping in BET.

I am really grateful to my lab members Parth, Tinku and Samitha for creating a healthy and cheerful environment in the lab and also for being there for me whenever I needed their help. I would also like to thank my seniors Damiota, Shikha and Joyal for their guidance.

I feel blessed to have all my friends especially Deepu, Balu, Aswathy, Anna and Rintu in my life. Their love and support keeps me happy always. My deepest gratitude to my parents and family for their unconditional love and trust.

Above all I want to thank God for everything, let love and peace spread everywhere.

## Notations and Abbreviations

<b>PNC</b>	Perovskite Nano Crystals
<b>RT</b>	Room Temperature
<b>DMF</b>	Dimethyl formamide
<b>MnCl<sub>2</sub></b>	Manganese Chloride
<b>PbCl<sub>2</sub></b>	Lead chloride
<b>CsCl</b>	Cesium chloride
<b>Mn</b>	Manganese
<b>Pb</b>	Lead
<b>Cl</b>	Chlorine
<b>Br</b>	Bromine
<b>I</b>	Iodine

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## Abstract

Metal halide perovskites are a new class of compounds which has intrinsic defect tolerant property and belong to a group of bright emitters. Through this project we are investigating a new pathway for the synthesis of Mn doped CsPbCl<sub>3</sub> perovskites nanocrystals, that is, Mn doped CsPbCl<sub>3</sub> perovskites are successfully synthesized on a mesoporous alumina film. The developed perovskite films maintain uniformity over the film which in turn can be used for several optoelectronic purposes. Detailed characterizations including UV-Vis, Photoluminescence studies, XRD, ICP-MS, BET adsorption studies were carried out to study the formed Mn doped CsPbCl<sub>3</sub> perovskite.

# Chapter 1

## Introduction

### 1.1 Perovskites

Perovskites are compounds with chemical formula  $ABX_3$ . A is an organic/inorganic monovalent cation (MA-methyl ammonium, FA-formamidinium, Cs-cesium, Rb-rubidium), B is a divalent metal cation ( $Pb^{2+}$ ,  $Sn^{2+}$ ,  $Ge^{2+}$ ) and X is a halide anion ( $Cl^-$ ,  $Br^-$ ,  $I^-$ ). Figure 1 shows the pictorial representation of the arrangement of the atoms in a cubic crystal.

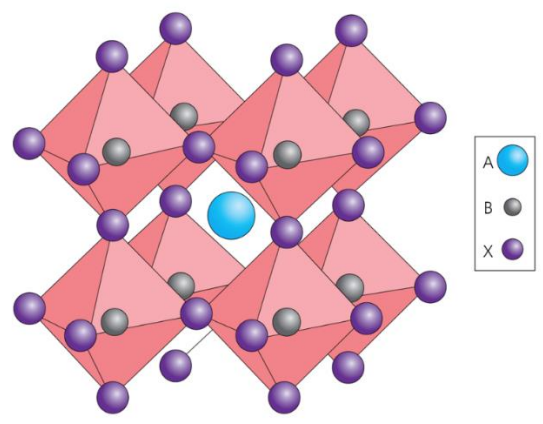


Fig1:  $ABX_3$  cubic crystal arrangement of cations and anions (Figure reproduced from reference1)

Metal halide perovskite has been in the spotlight of bright emitters which spans the entire visible region of the electromagnetic spectrum. Protesque et al<sup>2</sup> for the first time reported novel synthesis of cesium lead halide inorganic perovskite nanoparticles with a PL-QY of 90%. Colloidal cesium lead halide QDs have driven immense interest on research due to their optoelectronic properties and defect tolerant nature. The dangling bonds on the surface of the nanocrystals which are non-bonding in nature gives rise to defect states which can trap charge carriers inhibiting the optoelectronic processes. Structural defects in semiconductors leads to a



condition called defect states inside the energy bandgap, which act as trap states. The rare situation where intrinsic defects do not act as electronic trap states is called defect-tolerance.<sup>3</sup> Intrinsic defects do not act as a charge trapping site in perovskites due to its electronic band structure. Perovskite materials have defect tolerance because these materials mostly form defect states within the valence band or conduction band. They have less prone to form defect states within the bandgap. Defect states within the valence band or conduction band does not lead to non-radiative transition, but defect states within the bandgap greatly does. Defect states within the valence band or conduction band arises due to very unusual band structure of perovskite materials.

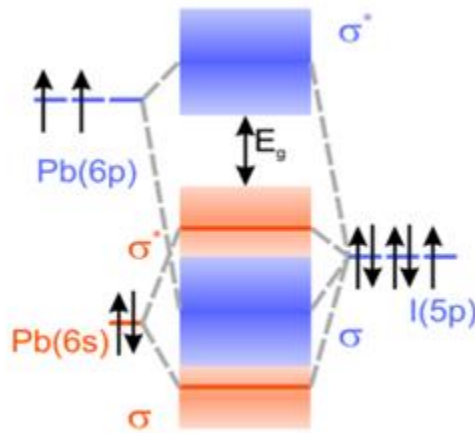


Fig 2: Defect-tolerant band structure (Figure reproduced from reference 3)

Bandgap of these materials are generally formed between two antibonding molecular orbitals. Fig 2 shows Pb (6s) - I (5p) and Pb (6p) – I (5p) antibonding molecular orbitals in case of APbI<sub>3</sub> type of perovskites which forms valence band maximum and conduction band minimum. In addition the strong spin-orbit coupling stabilizes the formed conduction band minimum.<sup>4-17</sup> These two aspects reduces the formation of defect states in perovskites and hence proves to be a better option than the conventional Quantum Dots. The tunable optical properties of the

perovskite nanocrystals are attributed to their permissible compositional modifications, size and shape.

## 1.2 Colour tunability in the Perovskite Nanocrystals (PNC)

Changing the composition of halide and doping with other metal ions are the common means of achieving colour tunability in PNC.

### 1.2.1 Halide exchange method

Halide exchange can be used to tune the NC composition, allowing very fine control of the  $\text{CsPbX}_3$  NC band gap while retaining both NC morphology and high PL quantum yield (QY). This tunability gives  $\text{CsPbX}_3$  NCs unique advantages over other NC materials for use in color selectable narrow-line-width LEDs and low-threshold lasers based on single and multiphoton pumping. Solution based colloidal synthesis of mono-dispersed 4-15 nm  $\text{CsPbX}_3$  pure halide and mixed halide composites with cubic phase perovskite crystal structure and cubic shape has been reported with high PL-QY of 50-90%.<sup>18</sup>

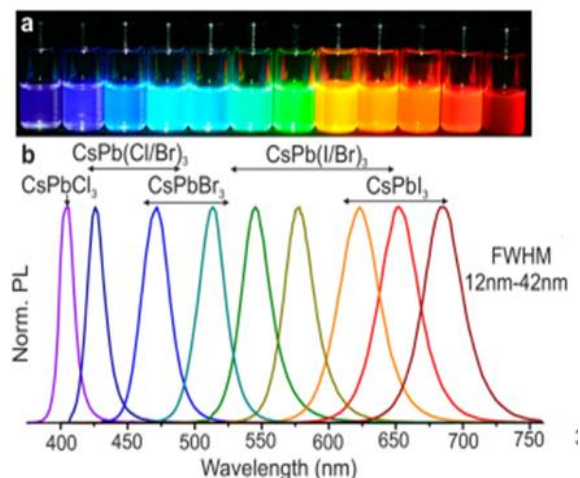


Fig 3: Colloidal perovskite  $\text{CsPbX}_3$  NCs ( $X = \text{Cl}, \text{Br}, \text{I}$ ) exhibiting tunable bandgap energies covering the entire visible spectral region (a) colloidal solutions in toluene under UV lamp ( $\lambda = 365 \text{ nm}$ ) (b) representative PL spectra ( $\lambda_{\text{exc}} = 400 \text{ nm}$  for all but  $350 \text{ nm}$  for  $\text{CsPbCl}_3$  samples. (Fig reproduced from reference 18)

Highly efficient photoluminescence (PL) tunable over the entire visible spectral range can be achieved by control over NC size and anion identity. Intriguingly, it has been shown that due to the high mobility of anions in the relatively open perovskite crystal structure, halide exchange can be used to tune the NC composition, and this tunability gives CsPbX<sub>3</sub> NCs unique advantages over other NC materials for use in color selectable narrow-line-width LEDs and low-threshold lasers based on single-and multiphoton pumping.<sup>18</sup>

### 1.2.2 Doping with metal ions

Doping with transition metal ions has been extensively explored as a way to introduce new optical, electronic, and magnetic properties, making them much more functional than their undoped counterparts.<sup>19</sup> An additional level of control over the electronic and optical properties of NCs be afforded by the incorporation of metal ions. The most commonly used metal dopants to date are Mn<sup>2+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, and Co<sup>2+</sup>. Doping semiconductor NCs with Mn<sup>2+</sup> has been particularly widely studied because it potentially imparts both novel magnetic and optical properties.

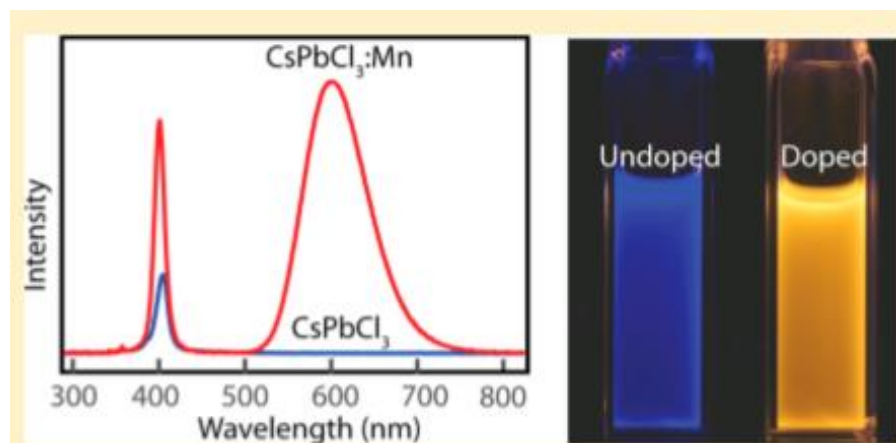


Fig 5: Photoluminescence of Mn-doped and undoped CsPbCl<sub>3</sub> nanocrystals & photographs of the sample under UV excitation. . (Figure reproduced from reference 19)

Substitutional isoelectronic doping of MX (M = Cd, Zn, X = S, Se) quantum dots with paramagnetic transition metal ions such as  $\text{Mn}^{2+}$  can generate intense sensitized dopant luminescence and create a magnetically coupled exciton state enabling optical control of magnetism or production of energetic hot electrons.<sup>19</sup> These new properties which results in the exchange coupling between the charge carriers of the host semiconductor and d electrons of the dopant, of a Mn-doped quantum dot opens a new pathway for energy exchange or forms new coupled electronic states between the exciton and dopant. New optical, electronic, and magnetic properties also arises in  $\text{CsPbX}_3$  perovskite semiconductor nanocrystals, similar to Mn-doped quantum dots, when  $\text{Mn}^{2+}$  ions is doped in  $\text{CsPbX}_3$  nanocrystals stably with sufficiently strong exchange coupling between the charge carriers.

### 1.3 Mn doping in Perovskite Nanocrystals

Doping NCs with  $\text{Mn}^{2+}$  has been particularly widely studied and gained much interest because it is stable and can replaces  $\text{Pb}^{2+}$  to a good extent. Fig 6 shows the atomic model of a typical Mn: $\text{CsPbCl}_3$  crystal where  $\text{Mn}^{2+}$  doping has happened which leads to replacement of  $\text{Pb}^{2+}$  by  $\text{Mn}^{2+}$  in the crystal structure.

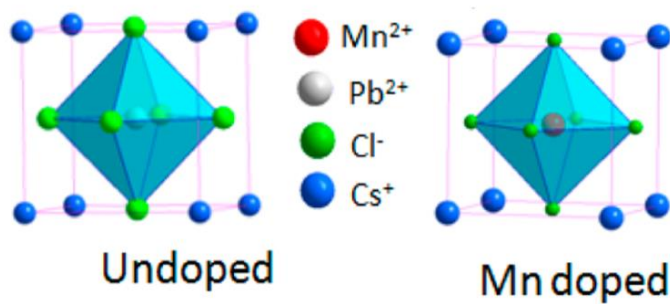


Fig 6: Atomic model showing a Mn doped  $\text{CsPbCl}_3$  crystal where  $\text{Mn}^{2+}$  is placed in the position of  $\text{Pb}^{2+}$  (Figure reproduced from reference 20)

It also introduces a new emission peak due to an internal  ${}^4T_1$  to  ${}^6A_1$  transition of the Mn ion. Band position of CsPbCl<sub>3</sub> and Mn d states are shown in Fig.7. Doping with Mn<sup>2+</sup> can generate intense sensitized dopant orange luminescence, hence we can use for several optoelectronic purposes. Doping NCs with Mn<sup>2+</sup> also imparts both novel magnetic and optical properties, due to strong exchange interactions of the 5/2 Mn<sup>2+</sup> spin with conduction and valence band carriers.<sup>21</sup>

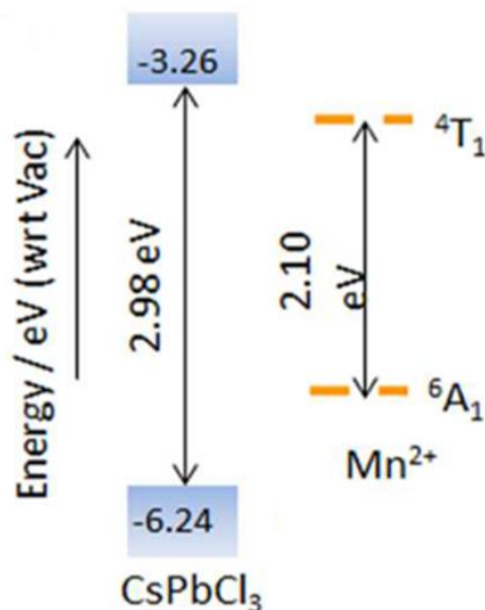


Fig 7: Band position of CsPbCl<sub>3</sub> and Mn d-states (Figure reproduced from reference 20)

## 1.4 Existing Methods

### 1.4.1 Hot injection method

PbCl<sub>2</sub>, MnCl<sub>2</sub>·(H<sub>2</sub>O)<sub>4</sub>, in Octadecene (ODE) along with Oleic Acid (OA) & Oleyl Amine (OAm) were added to a 25-mL 3 neck round bottom flask and were evacuated and refilled with N<sub>2</sub>. The solution was heated to 120 °C for 30 minutes and then was increased to 165 °C and later to 200 °C for 10 minutes each. At 200 °C, dried OAm and dried OA were subsequently injected to solubilize the solution. Then the Cs-oleate was swiftly injected and after 1 minute the solution was cooled with an ice bath. The NCs were precipitated with acetone and then centrifuged followed by dissolving in hexane.

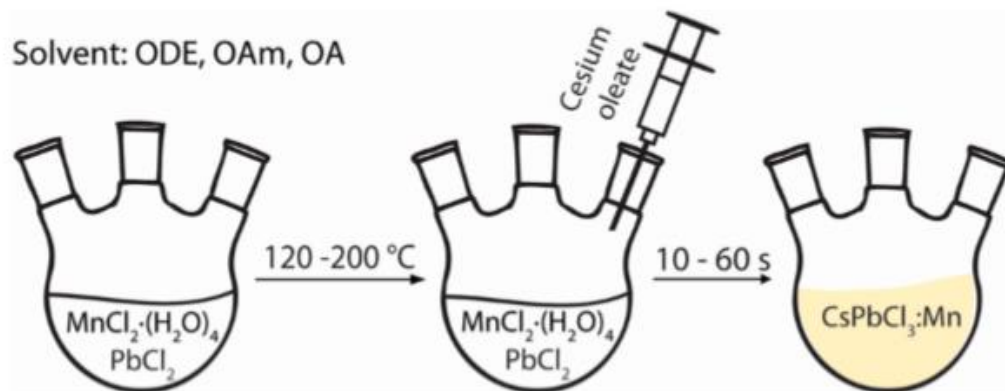


Fig 8: Schematic Representation of Synthetic Procedure for Mn-Doped  $\text{CsPbCl}_3$  by hot injection method (Figure reproduced from reference 19)

#### 1.4.2 Room temperature synthesis (LARP)

$\text{PbCl}_2$  and  $\text{CsCl}$  were dissolved in DMF, Oleic Acid (OA) & Oleyl Amine (OAm) were added to stabilize the precursor solution under vigorous stirring.  $\text{MnCl}_2$  was dissolved in DMF separately and 0.1 mL of the  $\text{MnCl}_2$  solution along with 1 mL of  $\text{PbCl}_2/\text{CsCl}$  solution was simultaneously injected into toluene under intense stirring. Large particle were removed from the crude solution by centrifuging at 4500 rpm for 5 minutes. Then, 4 mL of acetonitrile was added into the supernatant followed by 10000 rpm centrifugation. After that, the precipitates were dispersed in hexane. This method is also known as LARP (Ligand Assisted Reprecipitation)

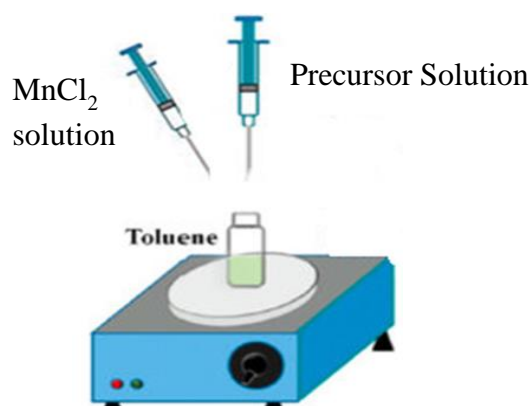


Fig 9: Schematic representation of room temperature synthesis for Mn-Doped  $\text{CsPbCl}_3$  (Figure reproduced from reference 22)

## 1.5 Objectives of my work

Research work on Mn doping in PNC has been successfully done by hot injection method and room temperature method. These methods has its own pros and cons. The advantage of hot injection method is Mn doped  $\text{CsPbX}_3$  NCs can be synthesized with different shapes and sizes and with good luminescence and the disadvantages are very high temperature is used for the synthesis and this method requires vigorous purification process. Size and shape of the PNC changes from batch to batch. The advantage of LARP method is Mn doped PNC can be synthesized in room temperature and the disadvantages are it requires vigorous washing, and purification is very tricky, that is separation of bigger and smaller NCs are required and at last only very small amount of crystals are obtained. This lead us to investigate a new pathway for the generation of Mn doped  $\text{CsPbCl}_3$  perovskite nanocrystals inside mesoporous matrix in thin film form. The advantages of this method are, it is a mesopore confined synthesis that is a strained mesopore atmosphere facilitates the formation of NC. For the formation of NC neither additional reagents (stabilizing agents) are required nor vigorous /tricky washing procedure is followed. Above all this could be synthesized in room temperature, everything is done in ambient atmosphere.

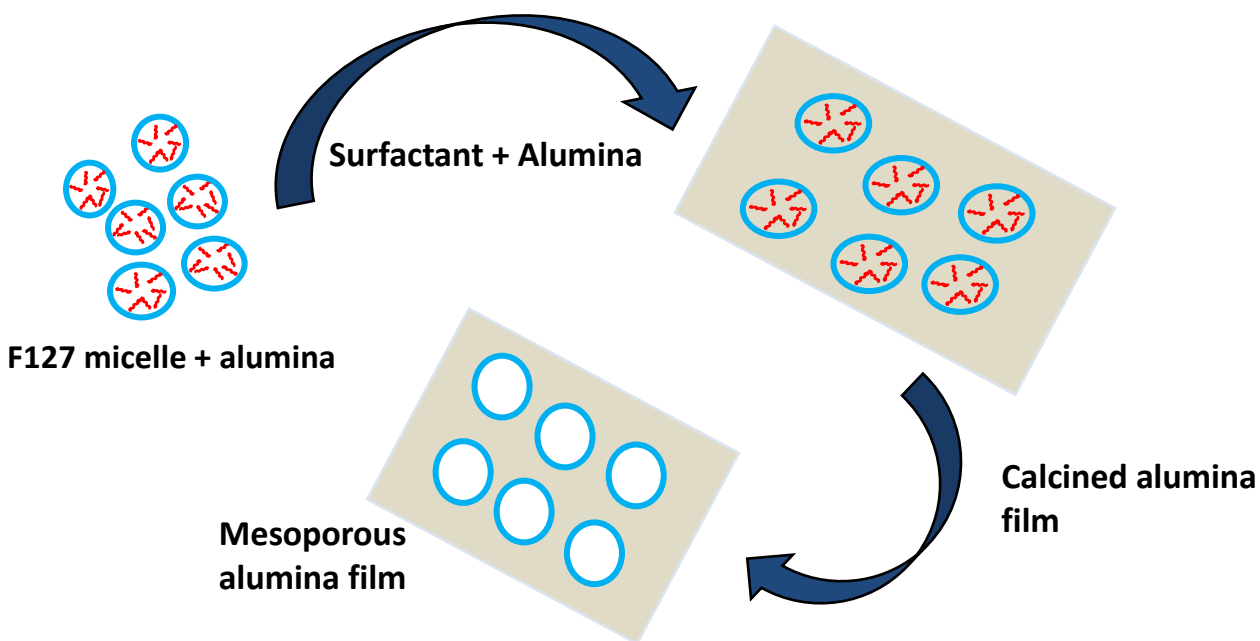


Fig 10: Schematic representation for the formation of mesoporous alumina film

# Chapter 2

## Experimental Section

### 2.1 Chemicals

ASB (Aluminium trisecondary butoxide) (Sigma Aldrich), Lead chloride ( $\text{PbCl}_2$ ) (Alfa Aesar), Cesium chloride ( $\text{CsCl}$ ) (SRL), Manganese chloride ( $\text{MnCl}_2$ ) (Sigma Aldrich), Hydrochloric acid ( $\text{HCl}$ ), 37% in water (MERCK), Absolute ethanol ( $\text{EtOH}$ , 99.9%) (Changshu Hongsheng Fine Chemicals), F-127 (Sigma Aldrich), N.N dimethyl formamide (Spectrochem).

### 2.2 Precursor synthesis

Lead chloride was prepared by dissolving in DMF solution.  $\text{CsCl}$  was dissolved in an ethanol water mix and  $\text{MnCl}_2$  was dissolved in ethanol solution.

### 2.3 Boehmite preparation

For preparation of boehmite sol, Yoldas method was followed which involves hot hydrolysis ( $>80^\circ\text{C}$ ) of ASB and subsequent peptization of boehmite precipitates using  $\text{HCl}$ . 10 g ASB (1 mol) was poured in 73 g hot water (100 mol) and stirred vigorously at  $80^\circ\text{C}$  under refluxing condition for 5 hours. After 1 hour a peptization process was performed by adding 0.40g of  $\text{HCl}$  and was stirred vigorously for another 5 hours. After 5 hours the solution was made to reflux for 30 hours without stirring at a temperature of greater than  $80^\circ\text{C}$ . Finally, a transparent solution was obtained which was ready for making the coating sol.

### 2.4 Coating sol preparation

The gel forming sol was prepared using the synthesized boehmite  $\text{AlO}(\text{OH})$ . The obtained solution was concentrated to 7.5 equivalent weight % of  $\text{AlO}_{1.5}$  using a rotatory evaporator to distill off  $2^\circ$  butanol along with some water. Methanol was added to dilute the  $\text{AlO}_{1.5}$  to 5.3



weight %. Surfactant F127 (PEOPPOPEO) was weighed 0.001mol % equivalent to the amount of  $\text{AlO}_{1.5}$  present in the sol and dissolved in 1-propanol. The 5.3 weight % sol was then added to the solution of the surfactant to make a final  $\text{AlO}_{1.5}$  which was of 4 weight % solution and then stirred for 1 hour. This was aged for 1 day at RT.

## **2.5 Coating sol preparation process**

Glass slides used for coating the alumina sol ( $25.4\text{mm} \times 76.2\text{mm} \times 1.2\text{mm}$ ) was first of cleaned very well with detergent and water, then it was washed with deionized water and then in ethanol and then boiled in 2-Propanol for about 5 minutes. The prepared alumina sol was now in a gel like form, hence it was stirred to make it into a solution form and with the help of a dipcoater, the cleaned glass slides were coated in this sol with a dipping rate 160 mm/min and a pulling out rate of 140 mm/min. The alumina coated slides were then dried in oven for about 15 min at 60 and then subjected to calcination in a tubular furnace at a control heating of 1 till 500 and made to calcine at this temperature for 1 hour. After this slides were cooled down by keeping outside in a natural way.

## **2.6 Perovskite preparation**

To prepare Mn doped  $\text{CsPbCl}_3$  perovskites, the alumina coated glass slides were first dipped in 0.025M concentration of lead chloride ( $\text{PbCl}_2$ ) dissolved in N.N dimethyl formamide (DMF) and dried in oven at 60 for 10 min. Now this was cooled to RT and then dipcoated with second precursor solution which was 0.1M cesium chloride salt ( $\text{CsCl}$ ) prepared in ethanol water mix. This was dried in oven at 60 for 3min. After cooling to room temperature this was dipped with third precursor solution, that is 0.018M  $\text{MnCl}_2$  dissolved in ethanol. After dipcoating with  $\text{MnCl}_2$  solution this was dried in oven at 60 for 3 min. Orange colour luminescent slides were formed thus indicating the formation of perovskite (this was done for 75% Mn doping in  $\text{CsPbCl}_3$  perovskites). Different percentage of Mn doping was also done.

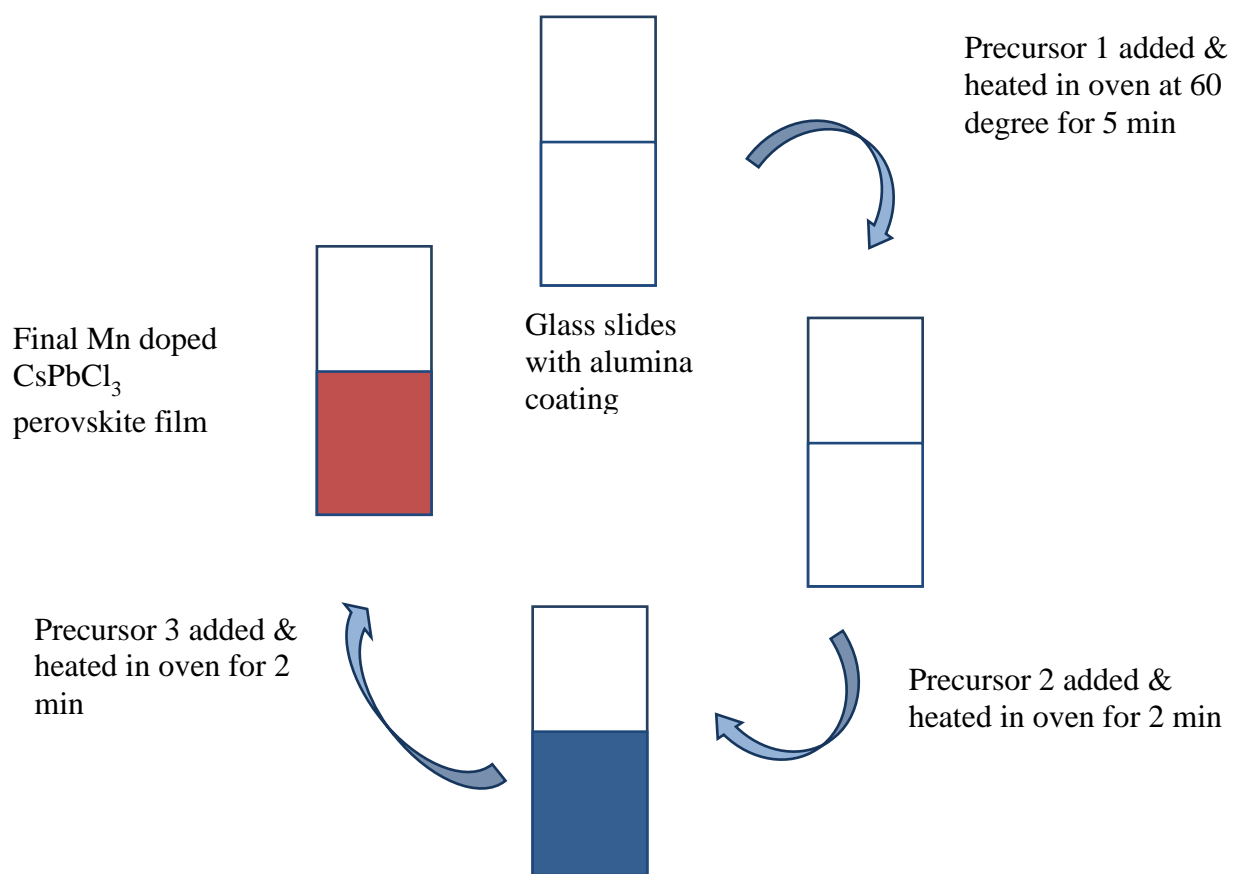


Fig 11: Schematic representation of formation of Mn doped PNC in a mesoporous alumina film.

## **2.7 Materials characterization**

### **2.7.1 Powder X-Ray Diffraction**

Powder X-ray diffraction was performed on thin films using X ray Diffractometer machine from Rigaku Ultima company IV company fully automatic high resolution system equipped with a 3kW sealed tube Cu K $\alpha$  X-ray radiation (generator power settings : 40kV and 40mA) and DTex Ultra detector using parallel beam geometry. The alumina coated glass slides were analysed over an angle range from 10 $^{\circ}$  to 70 $^{\circ}$  at a scan rate of 1 $^{\circ}$ /min.

### **2.7.2 UV-Visible Spectroscopy**

The UV-Visible spectra of all the films was recorded by using UV 3000+ LABINDIA spectrophotometer, at the scan rate 1nm/s (medium speed scan) and wavelength of window of 350nm - 800nm. Baseline correction was done with alumina coated slide.

### **2.7.3 Photoluminescence**

Photoluminescence (PL) spectra was recorded using Horiba Flluromax-4 with slit width of 1.5nm  $\times$  1.5nm with a scan integration time of 0.3s. The excitation wavelength  $\lambda_{ex}$  = 360nm for every samples.

### **2.7.4 Brunauer-Emmett-Teller (BET) adsorption study**

Mn doped CsPbCl $_3$  slides and Undoped slides prepared in alumina coated slides were scratched to make a comparison of the pore volume occupancy by BET analysis of surface area and BJH (Barrett - Joyner – Halenda) pore size distribution calculation. The Nitrogen adsorption-desorption isotherms were obtained with BET Bellmini instrument and BJH method was used to calculate the poresize distribution of the doped and undoped samples in alumina coated films.

### **2.7.5 Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)**

Mn doped CsPbCl<sub>3</sub> slides prepared in alumina coated slides were scratched off for analysis in ICP-MS. Objective is to do a comparison of amount of Mn obtained in the product NCs measured using ICP-MS, with that taken as precursor for doping.

# Chapter 3

## Results and Discussion

Different process were carried out to find the way to form NC inside the mesoporous matrix. First all the precursor solutions were mixed together and impregnated on mesoporous matrix. It didn't show any luminescence. Table 1 shows dipping the solutions in different order which lead to optimize the way of dipping the mesoporous matrix.

Table 1

Precursor 1	Precursor 2	Precursor 3	Observation
CsCl	PbCl <sub>2</sub>	MnCl <sub>2</sub>	No formation
CsCl	MnCl <sub>2</sub>	PbCl <sub>2</sub>	No formation
MnCl <sub>2</sub>	CsCl	PbCl <sub>2</sub>	No formation
MnCl <sub>2</sub>	PbCl <sub>2</sub>	CsCl	No formation
PbCl <sub>2</sub>	MnCl <sub>2</sub>	CsCl	No formation
PbCl <sub>2</sub>	CsCl	MnCl <sub>2</sub>	Orange Luminescence

Table 1: Sequence of the solutions used for dipping in formation of the PNC.

Thus the way of dipping for the formation of NC was optimized and table 2 shows varying the concentration of different precursor to get the best luminescence.

Table 2

<b>PbCl<sub>2</sub></b>	<b>CsCl</b>	<b>MnCl<sub>2</sub></b>
0.05 M	0.05 M	0.025 M
0.05 M	0.025 M	0.025 M
0.05 M	0.025 M	0.037 M
0.05 M	0.1 M	0.025 M
0.025 M	0.025 M	0.0125 M
0.025 M	0.025 M	0.0187 M
0.025 M	0.05 M	0.0125 M
0.05 M	0.025 M	0.025 M
0.025 M	0.05 M	0.018 M
0.05 M	0.025 M	0.037 M
0.05 M	0.05 M	0.025 M
0.05 M	0.05 M	0.037 M
0.025 M	0.1 M	0.0125 M
0.025 M	0.1 M	0.0187 M

Table 2: Variation in the concentration of precursor solution used for the formation of PNC.

The concentration of the precursors were varied from 0.025M to 0.1M and it was noted that slides gave bright luminescence when the concentration of CsCl was 0.1 M and concentration of PbCl<sub>2</sub> was 0.025 M.

### 3.1 Brunauer – Emmett – Teller surface area analysis

This study was done to understand the surface area and pore size distribution of the undoped (without Mn doping, only CsPbCl<sub>3</sub> PNC in mesoporous alumina matrix) and the doped (Mn doped CsPbCl<sub>3</sub> PNC) samples. This gave us an idea about occupancy of pores by Mn doped perovskites and undoped perovskites inside mesopores.

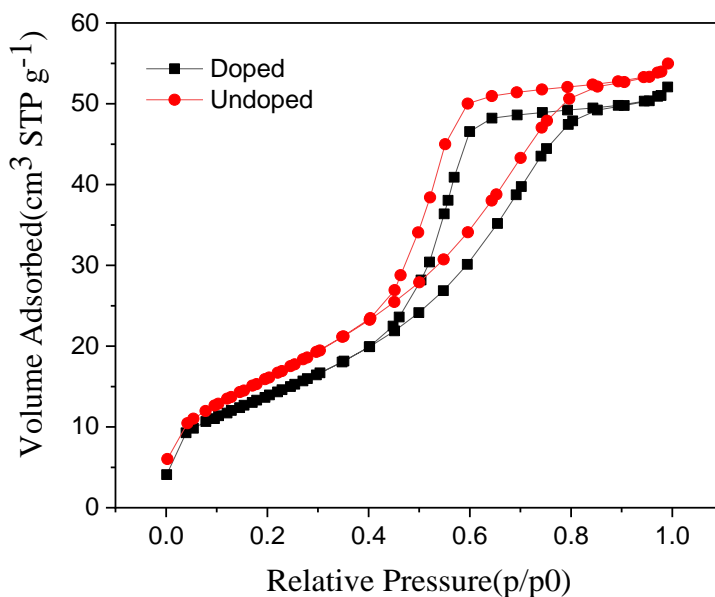


Fig 12: N<sub>2</sub> adsorption/desorption isotherm of undoped and doped samples

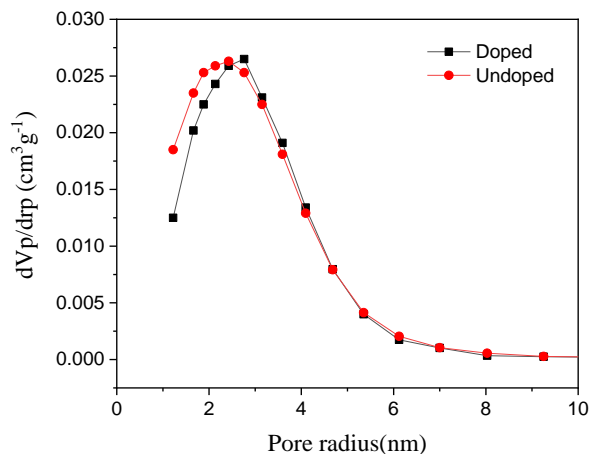


Fig 13: Pore size distribution of undoped and doped samples

N<sub>2</sub>-Sorption analyses were performed to evaluate the surface area and the porosity of the Mn doped CsPbCl<sub>3</sub> perovskites and as well as the CsPbCl<sub>3</sub> perovskite NCs film. From the hysteresis loop of the desorption isotherm, the existence of bottleneck pores can be understood. This facilitates the trapping of perovskite precursor solutions inside the pores. Surface areas of Mn doped CsPbCl<sub>3</sub> perovskites and as well as the CsPbCl<sub>3</sub> perovskite NCs film were found to be 63.218 (m<sup>2</sup>g<sup>-1</sup>) and 71.148 (m<sup>2</sup>g<sup>-1</sup>) respectively. The decrement in the surface area indicates the filling of pores by MnCl<sub>2</sub>.

Table 3

Sample details	Surface area(m <sup>2</sup> g <sup>-1</sup> )	Average pore diameter(nm)
Undoped CsPbCl <sub>3</sub>	71.148	5.51
Mn-doped CsPbCl <sub>3</sub>	63.218	6.14

Table 3: Surface area and pore volume of undoped and doped samples.



### 3.2 Powder X-Ray diffraction analysis (PXRD)

PXRD data shows formation of cubic PNCs of Mn doped and undoped  $\text{CsPbCl}_3$  where the peaks are centered around  $2\theta = 16.09$  for (100), 22.8 for (101), 24.7 for (110), 32.1 for (200), 36.2 for (210), 39.6 for (211), 46.0 for (220). There was a small shift in the peak from undoped to doped.

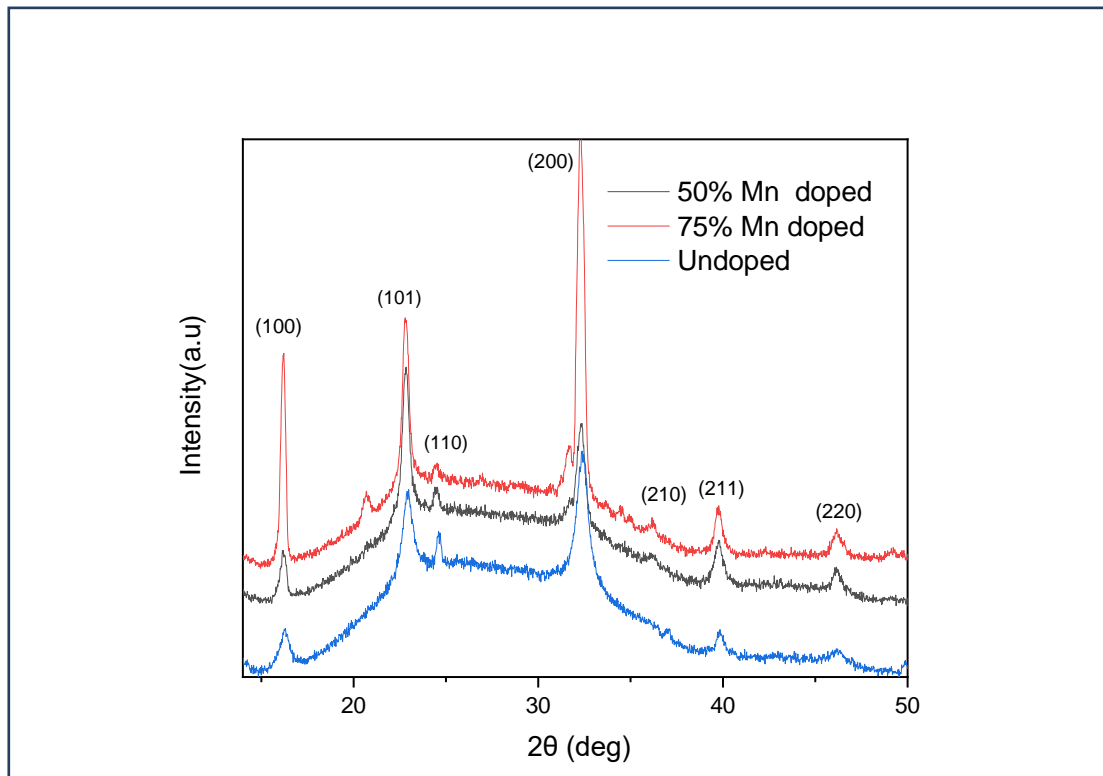


Fig 14: PXRD data of undoped, 50% Mn doped and 75% Mn doped samples

### 3.3 Photoluminescence Spectroscopic Study & UV Visible Study

The absorption spectra of the host perovskite nanocrystals show only a minor changes at different doping concentrations, indicating the relatively weak effect of the doped  $Mn^{2+}$  ions on the electronic structure of the host nanocrystals. After Mn doping, a new emission peak arises at 595nm which is a characteristic peak of Mn dopants. The excitonic PL intensity decreases because of the excitonic energy transfer to  $Mn^{2+}$  ions, exciting the  $Mn^{2+}$  ions from a high-spin  ${}^6A_1$  state to a lower-spin  ${}^4T_1$  state. The de-excitation process from  ${}^4T_1$ – ${}^6A_1$  state gives rise to the orange emission with peak at 595 nm. Figure 15 shows UV visible and PL of different samples.

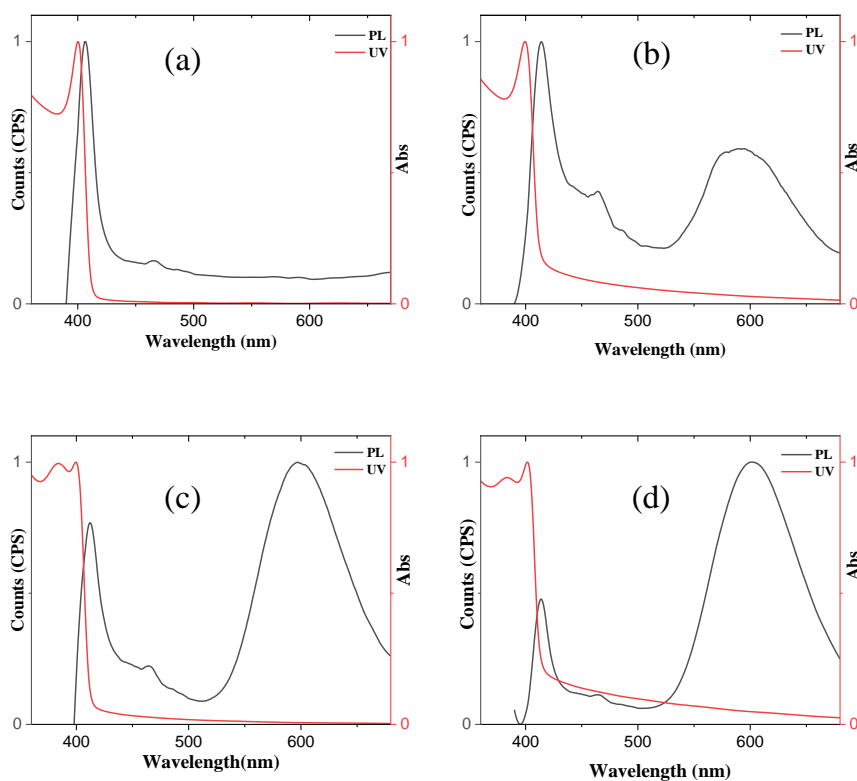


Fig 15: UV visible & PL spectra of (a) undoped  $CsPbCl_3$  and various concentration (b) 25% Mn doped  $CsPbCl_3$  (c) 50% Mn doped  $CsPbCl_3$  (d) 75% Mn doped  $CsPbCl_3$

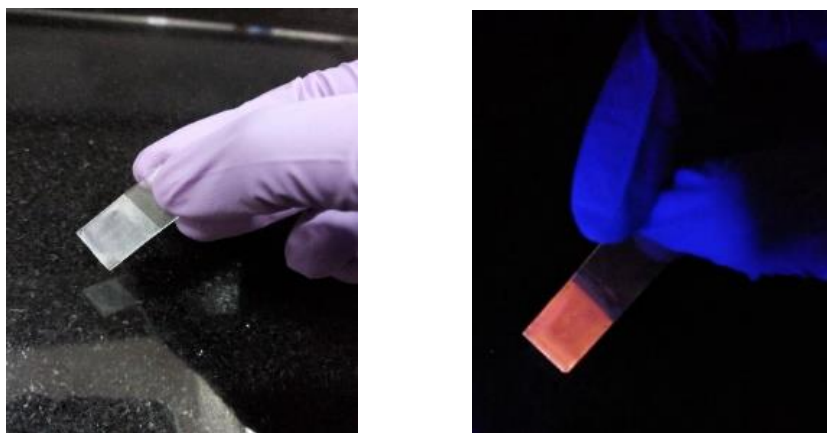


Fig 16: Digital photo of the Mn doped  $\text{CsPbCl}_3$  NC in alumina coated glass slide films under daylight and UV light

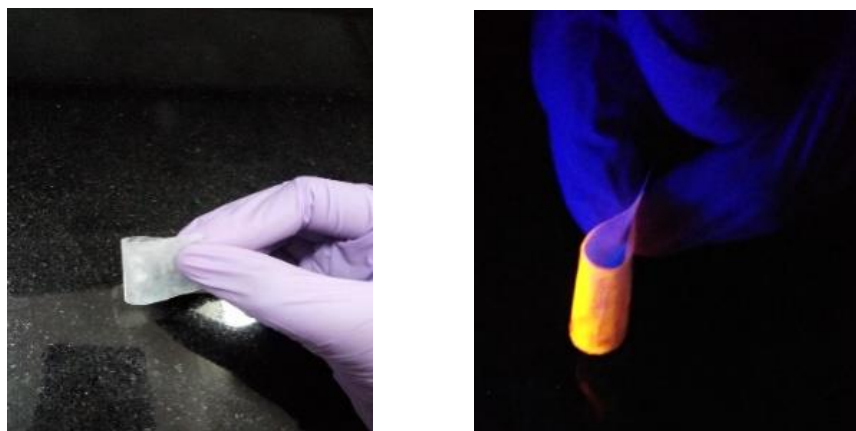


Fig 17: Digital photo of Mn doped  $\text{CsPbCl}_3$  NCs in alumina composite film on flexible polypropylene substrate under daylight and UV light.

### 3.4 Inductively Coupled Plasma – Mass Spectroscopy

The 75% doped slides were scratched off to get the sample in a powder form and ICP-MS study was conducted.

Table 4

<b>% Mn precursor taken</b>	<b>% Mn from ICP-MS</b>
<b>75 %</b>	<b>29.4 %</b>

Table 4: Comparison of amount of Mn taken as precursor for doping, with that obtained in the product NCs measured using ICP-MS

75% of  $\text{Mn}^{2+}$  was doped on the  $\text{CsPbCl}_3$  perovskite nanocrystals and from the ICP-MS study it was understood that 29.4% of  $\text{Mn}^{2+}$  was incorporated inside the PNC. That is a considerable amount of  $\text{Mn}^{2+}$  gets doped in the PNC replacing  $\text{Pb}^{2+}$ .

### 3.5 Reproducibility

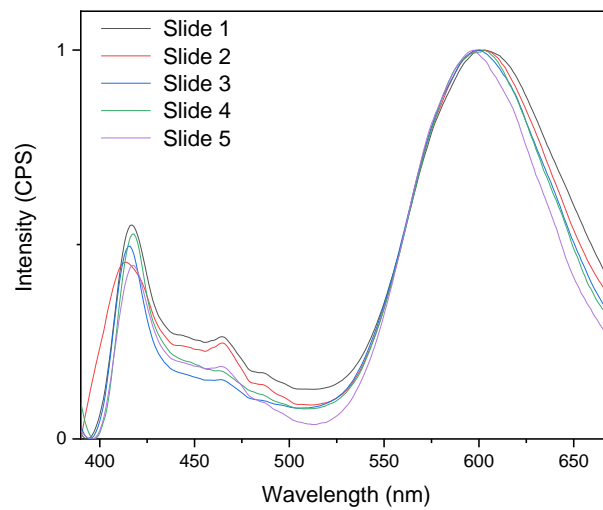


Fig 18: PL spectra taken of 5 different Mn doped slides

In order to check reproducibility, the 75% Mn doped slides were produced in 5 different alumina coated slides and PL spectra was taken. Mn doped perovskites were successfully reproduced in alumina coated films.

# Conclusion and Future Directions

Our investigation to synthesize Mn doped CsPbCl<sub>3</sub> perovskites on a mesoporous alumina film has been successfully done. The developed perovskite films maintain uniformity over the film which in turn can be used for several optoelectronic purposes. This could be done in room temperature and moreover there is no need of any stabilizing agent. Mn doped slides showed good PL spectra and they are reproducible.

Electron Paramagnetic Resonance (EPR) and Time-Correlated Single Photon Counting (TSCPC) Characterization also need to be done. This work can also be extended further by doping with different kind of metal ions.

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