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Article

Enhancing Stability and Emission in Metal Halide Perovskite Nanocrystals Through Mn²⁺ Doping

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Abstract Metal halide perovskite (MHP) nanocrystals (NCs) offer great potential for high-efficiency optoelectronic devices but suffer from structural softness and chemical instability. In this work, we synthesize Mn-doped methylammonium lead bromide (MAPbBr₃) NCs using the ligand-assisted reprecipitation method and investigate their structural and optical stability. X-ray diffraction confirms Mn²⁺ substitution at Pb²⁺ sites and lattice contraction. Photoluminescence (PL) measurements show a blue shift and a significant PL quantum yield enhancement, reaching 72% at 17% Mn²⁺ doping, a 34% increase over undoped samples, attributed to effective defect passivation and reduced non-radiative recombination, supported by time-resolved PL data. Mn²⁺ doping also improves stability under ambient conditions. Low-temperature PL reveals crystal phase transitions, while Mn²⁺ incorporation promotes self-assembly into superlattices with larger crystal sizes, better structural order, and higher superlattice density. These results demonstrate that Mn²⁺ doping enhances both optical performance and structural robustness, advancing the potential of MAPbBr₃ NCs for stable optoelectronic applications.

Keywords: Metal halide perovskite nanocrystals; quantum dots; Mn-doped methylammonium lead bromide; crystal phase transition; PLQY enhancement; perovskite stability; nanocrystal superlattices

1. Introduction

Metal halide perovskites (MHP) nanocrystals (NCs) or quantum dots are gaining significant interest owing to their intriguing optical and physical properties, including bandgap tunability via tuning NC size and chemical compositions, high radiative recombination rate, defect tolerance, high absorption coefficient, high photoluminescence (PL) quantum yield, long range coherent coupling, and strong Coulomb interaction.^{1–4} These excellent properties offer MHP NCs as building blocks for developing highly efficient optoelectronic devices, for example, light-emitting diodes,^{5,6} photodetectors,⁷ photovoltaic cells,^{8–10} lasers,^{11,12} single photon sources.^{4,13,14} Three dimensional MHPs generally have a structure of ABX₃, where A is a cation can be Cs⁺ or methylammonium CH₃NH₃⁺ (MA), B is divalent metal ion like Pb²⁺ or Sn²⁺, X is a halide anion (X = I, Br, Cl). At room temperature, the crystal adopts a cubic phase, consisting of a cubic array of corner-sharing BX₆ octahedra, with the A-site cation located within the cuboctahedral cavities. High yields can be achieved using established methods such as hot injection or ligand-assisted reprecipitation (LARP).^{15,16} The most common perovskite NCs are CsPbX₃ and MAPbX₃, because of their ease of synthesis. However, MHP structures are soft and chemically unstable, with dynamic and weak surface ligands binding, and susceptibility to anion-exchange reactions; their stability has always been a large concern and challenge. MHP NCs are affected by external factors such as light, humidity, ambient temperature, and proton exchange reactions, leading to a decrease in photoluminescence quantum yield (PLQY) over time, hindering their practical applications. Several strategies have been proposed and implemented to improve the optoelectronic performance of MHP NCs, such as surface passivation,

heterostructure formation, A-site doping, B-site doping, and core/shell structures.^{17–20} B-site doping is an effective strategy for enhancing the PLQY of MHP NCs, offering a straightforward synthesis process that preserves the integrity of the perovskite structure. In addition, B-site doping also enables the emergence of new physical phenomena and allows precise tuning of the optical and electronic properties of the material.^{20–26} Wang et al. doped Eu^{3+} into CsPbCl_3 , and the positions of typical emission bands were tuned by adjusting the Eu^{3+} ion doping amount.²⁷ In general, metallic ions such as Co^{2+} , Cu^{2+} , Mn^{2+} , Fe^{2+} , and rare earth ions are suitable for B-site dopants into MHP NCs, enhancing their optoelectronic properties hold promise for their applications in highly efficient opto-electronic devices.^{28–32} Among them, Mn^{2+} is the most sought-after due to its unique chemical and physical properties, such as exhibiting bright and stable PL, introducing magnetic and spintronic properties, and enhancing the optical stability of perovskite materials.^{21,22,33–36} Not all metallic ions can be doped into perovskites, with the structure ABX_3 the Goldschmidt tolerance factor, $t = \frac{r_A + r_B}{\sqrt{2}(r_A + r_B)}$, should be in the range of 0.76 – 1.13 to ensure the three-dimensional perovskite structure, where r_A and r_B are the radii of atom A and B, respectively.^{37,38} The doped metal species are also be constrained by the octahedral coefficient μ , defined by $\mu = r_B/r_X$, the stability range for μ is between 0.44 and 0.89.^{39,40} The incorporation of Mn^{2+} into the perovskite crystal lattice increases the tolerance factor, improves the structural stability, and enhances the radiation pathways.^{37,38} Liu et al. elucidated the role of the relative strengths Mn-Cl bond in the precursor and host lattice in incorporating Mn^{2+} ions into perovskite CsPbX_3 NCs. They successfully doped Mn^{2+} into CsPbCl_3 NCs and observed a dual-band emission, which is originated from the energy transfer between the Mn^{2+} ion and the host.⁴¹ In addition, cation dopants can suppress non-radiative (NR) recombination due to effectively passivating surface and structural defects, leading to an increase in the PLQY perovskite NCs.^{42,43} The mechanism of Mn^{2+} doping is explained through the dynamic exchange of cations and halogen anions. The homologous bond dissociation between Mn-X (halogen) and Pb-X is extremely important, which enables the successful substitution of Pb^{2+} by Mn^{2+} .^{44,45}

Most Mn^{2+} -doped MHP NCs, particularly CsPbBr_3 and CsPbI_3 , have been synthesized using a hot injection method. While this approach yields high-quality NCs, it requires high reaction temperature, precise control of temperature and reaction time, and poses significant challenges for scale-up. In this study, we synthesized Mn^{2+} -doped MAPbBr_3 NC using a simple method, ligand-assisted reprecipitation, at room temperature. We observed PLQY improvement in MAPbBr_3 NCs with Mn-dopant, reaching an optimal value of 72% at 17% Mn^{2+} , an increase of 34 % compared to the undoped sample. In addition, Mn^{2+} doping can passivate the defects of NCs, replacing the vacancy of cation sites without changing the structure of the perovskite material, resulting in significantly improved optical stability. To investigate the effect of Mn^{2+} on optical and structural stabilities, we monitor the long-term stability of the sample under ambient conditions, conduct optical properties at low temperature, and grow NC superlattices from non-doped and Mn-doped MAPbBr_3 NCs. The improvement of NCs quality by Mn^{2+} doping is a promising strategy to grow a superlattice of MAPbBr_3 NCs through a self-assembly process.

2. Materials and Methods

2.1. Materials

Lead (II) bromide (99%), methylamine bromide ($\text{CH}_3\text{NH}_2\text{Br}$), manganate (II) bromide (99%) n-octylamine ($\geq 99\%$), oleic acid ($\geq 90\%$), N,N-dimethylformamide (DMF), toluene, didodecyltrimethylammonium bromide (DDAB, 98%) were purchased from Sigma-Aldrich.

2.2. Synthesis of Mn-Doped MAPbBr_3 NCs

The method we used to synthesize $x\text{Mn-CH}_3\text{NH}_2\text{PbBr}_3$ NCs is ligand-assisted reprecipitation (LARP), where x is the mole percentage in the precursors. A combination of 0.2 mmol of $\text{CH}_3\text{NH}_2\text{Br}$, 0.2(1-x) mmol of PbBr_2 , and 0.2x mmol of MnBr_2 (x = 0, 0.05, 0.1, 0.15, 0.17, 0.2 and 0.25) were mixed

in 5 mL DMF with 40 μL oleylamine (OLA) and 400 μL oleic acid (OA) to generate a precursor solution in the standard manufacture of MAPbBr_3 NCs. After that, at room temperature, the precursor solution was injected into toluene at a 1:10 volume ratio. The reaction was kept for 10 minutes to form colloidal MAPbBr_3 NCs. The product was then centrifuged at 7000 rpm for 10 minutes. The large crystal size aggregated at the bottom was removed. The upper fraction was then further centrifuged at 20,000 rpm for 2 hours to discard the supernatant. The bottom containing NCs was then diluted in toluene to make a NC solution. Since the exact amount of Mn^{2+} incorporated into the perovskite lattice is unknown, we name the Mn-doped samples as $x\text{Mn-MAPbBr}_3$, where x is the molar ratio of Mn to the total (Pb+Mn).

2.3. Surface Passivation

A mixture of 9.2 mg dimethyldidodecylammonium bromide (DDAB) in toluene (2 mL) was prepared to have the solution of DDAB in toluene (0.01 M). 200 μL of the purified $x\text{Mn-MAPbBr}_3$ NCs and 10 μL DDAB solution (0.1 M) were mixed and stirred for 1 hour at room temperature.⁴⁶ Discard the supernatant and disperse the precipitate in 5 mL of toluene.

2.4. Preparation of NC Superlattice

$x\text{Mn-MAPbBr}_3$ ($x = 0$ and $x = 0.17$) NC solutions were used to form a superlattice by the self-assembly method through the gradual evaporation of the solvent. The square pieces of silicon substrate $\langle\text{P-111}\rangle$ $1\text{ cm} \times 1\text{ cm}$ were placed in a glass petri dish with a diameter of 90 mm. The NC solution was dropped onto the Si substrate with approximately 50 μL . To protect it from ambient light and air currents, the petri dish was covered with a glass lid and loosely wrapped in foil. The superlattice will be formed in about 8 to 10 hours.⁴⁶

2.5. Characterizations

X-ray diffractions (XRD) were recorded using an X-ray diffractometer (Rigaku, Cu $\text{K}\alpha$ with $\lambda = 1.54056\text{ \AA}$, 40 kV, and 40 mA). The samples were prepared by drop-casting NCs solution onto a silicon substrate, $\langle\text{P-111}\rangle$, for measurements.

Atomic force microscopy (AFM) imaging was performed to measure the thickness and morphology of MAPbBr_3 superlattice, using a silicon tip operated in semi-contact mode from NTEGRA Spectra II (NT-MDT Inc).

Photoluminescence (PL) confocal scanning: The measurement is equipped with a confocal laser microscope. The excitation and collection were used with a 100x long working-distance objective with a numerical aperture of 0.67. The sample is excited by the femtosecond laser pulses at a wavelength of 400 nm or 800 nm with a pulse duration of $<100\text{ fs}$ and a repetition rate of 80 MHz (Mai Tai, Spectra Physics). The PL image was captured using a Galvo mirror scanning system, and the PL signal was recorded via an EM-CCD camera.

Optical Spectroscopy: Absorption spectra were measured with a UV-VIS spectrophotometer (Shimadzu, RF-5301PC). A femtosecond laser pulse at 405 nm was used to excite the sample for PL spectral measurements. Using a 10x magnification objective for excitation and collection through a long-pass chromatic mirror and color filter, an Ocean Optics spectrometer was used for this measurement. Time-resolved photoluminescent (TRPL) dynamics were obtained using time-correlated single photon counting (TCSPC), PicoHarp300. The samples for PL and TRPL measurements were prepared by drop-casting of NC solution onto a silicon substrate.

3. Results and Discussion

3.1. Structural Characterization of Mn-doped MAPbBr_3 NCs

The one-pot synthesis of Mn-doped MAPbBr_3 perovskite NCs using ligand-assisted reprecipitation (LARP), was described in section 2.2. Briefly, a mixture of precursors including MABr,

PbBr₂, MnBr₂ (x molar fraction), OLA, and OA with the desired stoichiometric molar concentrations in a polar DMF solvent was injected into a non-polar anti-solvent toluene container under vigorous stirring at room temperature. The crystal grown is due to a reduction in solubility by anti-solvent, leading to supersaturation and fast nucleation, Fig. 1a. The ligands (OA, OLA) prevent uncontrolled aggregation, and provide colloidal stability and passivate the crystal surface. This synthesis method is simple, a room temperature process, and scalable. In the Mn-doped perovskite, Mn²⁺ substitutes for the Pb²⁺ cation site. The perovskite structure is maintained even though the cell size was decreased because of the smaller atomic size of Mn²⁺ compared to Pb. The shrinkage of the crystal lattice is reflected in a shift in the XRD pattern. The Mn²⁺ ions directly participate in the nucleation process to form MAPb_{1-y}Mn_yBr₃ NCs, within the limit of Mn²⁺ concentration, allowing the perovskite structure to be stable. This can be confirmed through the calculation of the tolerance factor and octahedral factor of the perovskite.^{37,38,47} These considerations reflect a trade-off between colloidal stability and the successful incorporation of Mn²⁺ ions.

Figure 1 presents the XRD patterns of xMn-MAPbBr₃ NCs for various Mn²⁺ concentrations. There are two strong diffraction peaks at around 15.2° and 30.4°, corresponding to the (100) and (200) for both pure and Mn²⁺-doped MAPbBr₃, confirming the cubic phase of perovskite crystal at room temperature.^{48,49} No secondary peaks were observed on the XRD patterns, and the shift in the XRD peaks confirms the effective incorporation of Mn²⁺ in the MAPbBr₃ lattice. The XRD peak shift increases with increasing doping concentration up to 20% of Mn²⁺, which indicates the incorporation of Mn²⁺ in the crystal lattice. It has been reported that doping can induce structural evolution, especially when the size mismatch between the dopant atom and the substituted atom is large, but the small distortion here shows that the lattice contraction and octahedral tilt are not strong enough to produce a discernible structural change.⁵⁰ The XRD peak shift to larger angle is shown in Fig. 1c with increasing dopant concentration because of the contraction of the lattice due to the replacement of higher crystal radii Pb²⁺ ions (1.12-1.19 Å) by smaller Mn²⁺ ions (0.8 Å).⁵¹⁻⁵³ The different behavior of the XRD shift at x = 0.25 presumably at high Mn²⁺ concentration, the Mn²⁺ ions do not substitute Pb²⁺ ions rather form segregated crystal phases of MAPbBr₃ and MAMnBr₃ which will lead to lower PLQY. Further research is needed to reveal crystal structures at high Mn²⁺ concentration.

At room temperature, the MAPbBr₃ crystal has the cubic phase, the lattice parameter *a* is calculated from the XRD peak (200) using the formula:⁵⁴ $a = d \cdot \sqrt{h^2 + k^2 + l^2}$, where (h k l) are the Miller indices, *d* is the interplanar spacing, which is calculated using Bragg's law $n\lambda = 2d \cdot \sin\theta$. In the XRD, θ is the diffraction angle and λ is the wavelength of the incident X-ray (1.54 Å for Cu K α), for the first order diffraction *n* = 1. In Fig. 1c, the calculated lattice parameter decreases with increasing Mn²⁺ concentrations, except for the 25% Mn²⁺ dopant. This indicates that the smaller dopant Mn²⁺ ions are substituting for Pb²⁺ ions, causing a contraction of the lattice. This observation is consistent with Vegard's law, which states that the lattice parameter changes linearly with composition in a solid.⁵⁵

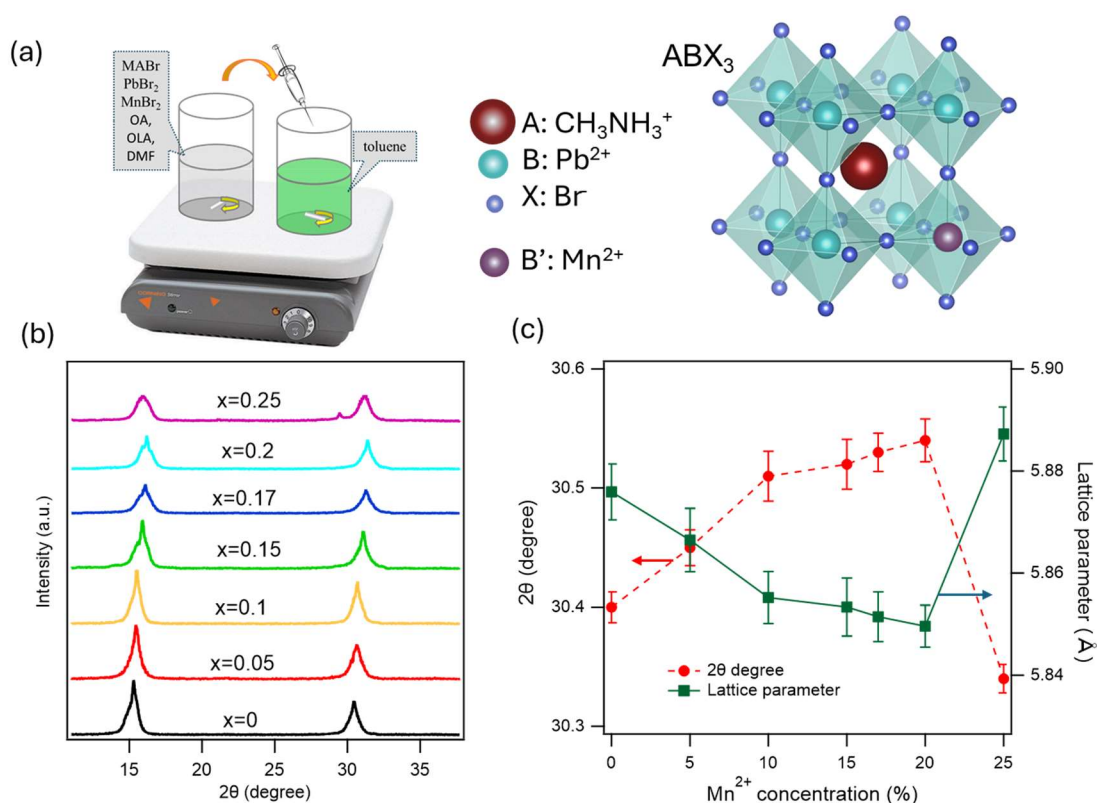


Figure 1. (a) Schematic of Mn-doped MAPbBr₃ NCs synthesis and the perovskite crystal structure. (b) XRD patterns of xMn-MAPbBr₃ NCs with different Mn²⁺ concentrations. (c) 2θ degree (red) at (200) plane and calculated lattice parameter (blue) as a function of Mn²⁺ concentration.

3.2. Optical Characterization of Mn-Doped MAPbBr₃ NCs

Figure 2 presents the optical characterizations of xMn-MAPbBr₃, with the Mn²⁺ concentration increasing from x = 0 to 0.25. We observe a gradual blue shift of the emission wavelength from 517 to 492 nm, in agreement with the previous observations.⁵⁶ The absorption, emission, and PLQY measurements were done on NCs in toluene solutions. The blue shift was attributed to the smaller size of NC due to the shrinkage of the crystal lattice when the smaller atomic size Mn²⁺ ions substituted for Pb²⁺. The reduction of the lattice constant of the cubic parameter was calculated from the XRD pattern, Fig. 1c, which indicates the Mn²⁺ ions are incorporated into the perovskite crystal by substituting Pb²⁺ ions. The incorporation of Mn²⁺ ions in the crystal lattice may also perturb the electronic band structure of the perovskite crystal, although it does not introduce new energy levels. While Mn-dopant into CsPbCl₃ introduced new energy level and dual band emission arises,^{21,57} the absence of Mn²⁺ emission in Mn-doped CsPbBr₃ or MAPbBr₃ is due to the negligible difference between ⁴T₁ to ⁶A₁ band gap of the d-state of Mn²⁺ ions and the transition band gap of pure APbBr₃ crystals.^{58–60}

As the Mn²⁺ doping concentration increases, the PLQY increases from 38% for the pure MAPbBr₃ to 72% for the 17 % Mn²⁺ concentration. Further increasing Mn²⁺ doping concentration results in a drop in the PLQY. At 25% of Mn²⁺, the PLQY is 49%, Fig. 2b. The significant PLQY enhancement with increasing Mn²⁺ concentration to MAPbBr₃ NCs indicates the efficient reduction of NR recombination pathways. It has been suggested that Mn²⁺ ions fill the Pb²⁺ vacancies and passivate dangling bonds and defects of crystal surface.⁵⁶ Further increasing the Mn²⁺ concentration above 20%, leads to a decrease of PLQY, possibly due to the strong distortion of the crystal lattice introducing new defects, or may result in the segregation phase of MAPbBr₃ and MAMnBr₃, forming domain boundaries and defects as the reverse change of the XRD shift, Fig. 1c.

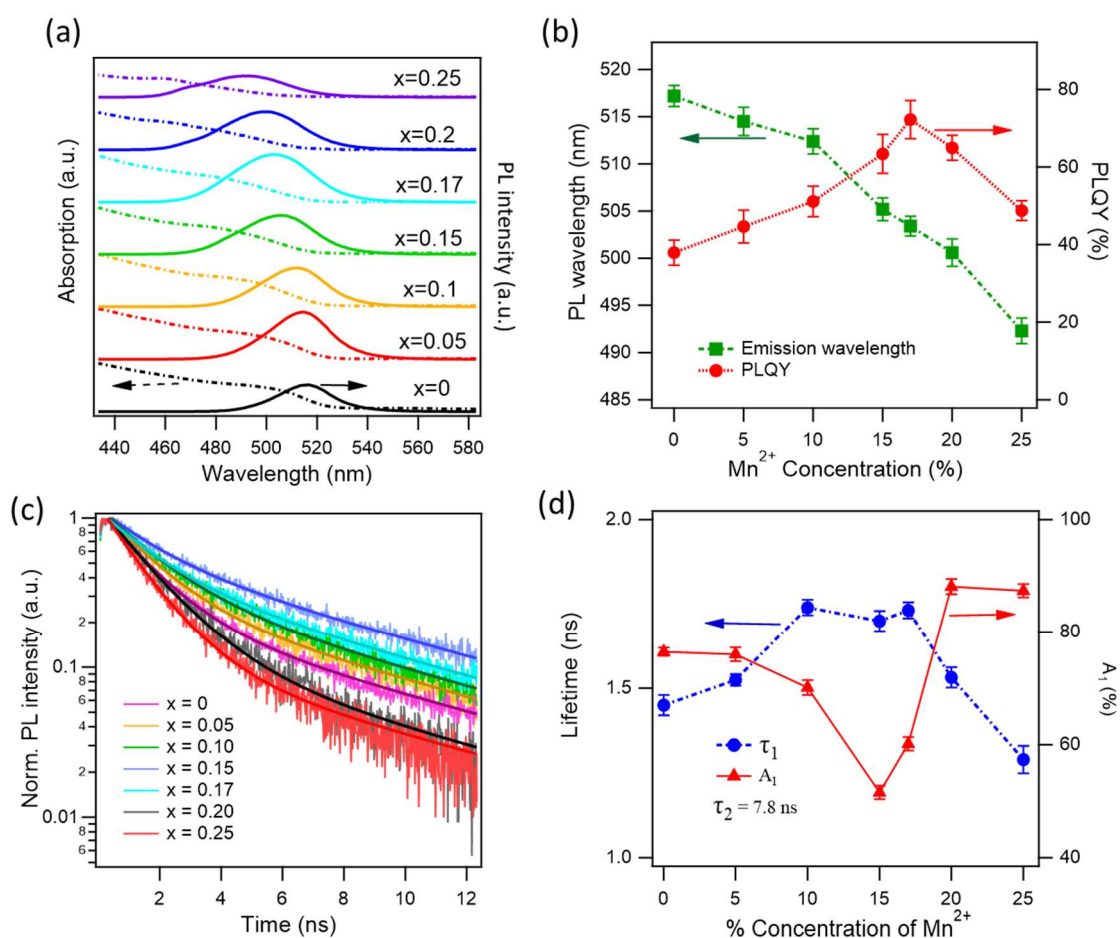


Figure 2. Optical characterizations of $x\text{Mn-MAPbBr}_3$ perovskite NCs. (a) Absorption (dashed) and emission (solid) spectra with the different Mn^{2+} doping concentrations. The PL spectra were measured at 400 nm excitation. (b) Mn^{2+} concentration dependence of the emission wavelength (green) and PLQY (red). (c) Normalized PL dynamics at 400 nm excitation, excitation pulse 100 fs. (d) Non-radiative lifetime (τ_1) and its amplitude percentages obtained from global fittings, the radiative lifetime was held the same for all fits. Fitted radiative lifetime returns a value of 7.8 ± 1 ns.

To have better insight into the reduction of NR recombination pathways induced by Mn^{2+} doping, we measure time-resolved PL (TRPL) dynamics at various Mn^{2+} concentrations, as shown in Fig. 2c. The measurements were performed on thin films, and the resulting dynamics reveal two decay time constants corresponding to radiative and NR recombination. For simplicity, we assume that the radiative rate remains constant across different Mn^{2+} concentrations. We performed global fitting of the dynamics, keeping the radiative lifetime fixed for all traces. The fit is used a biexponential function, $I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$, where (A_1, τ_1) and (A_2, τ_2) are the amplitudes and lifetimes of NR and radiative decay channels, respectively. The obtained fitting constants are displayed in Fig. 2d, the radiative lifetime is 7.8 ± 0.1 ns for all traces. The NR lifetime increases from 1.4 to 1.7 ns (at $x = 0.1, 0.15$, and 0.17), further increasing Mn^{2+} concentration results in the reduction of the NR lifetime. The radiative lifetime of excitons in perovskite NCs has been reported to be largely varying from a few to tens of ns, depending on the NC size and excitation conditions. The NR lifetime was reported to be ~ 1.5 ns, in agreement with our observation.^{61,62} The most important observation here is the percentage of NR amplitude constant, A_1 . This represents the weight of the NR channel. As can be seen, the weight of NR is 76% for non-doped NCs and drops to 51% at $x = 0.15$, and rises to $\sim 87\%$ at $x = 0.2$ and 0.25 . The lowest NR component at $x = 0.15$ is consistent with the maximum PLQY at $x = 0.17$. Indeed, the Mn^{2+} dopant at an optimal value reduces NR by infilling the Pb^{2+} vacancies and passivating defects/dangling bonds. It is worth noting that while the

PLQY measurements were performed on solution samples, the TRPL dynamics were measured on NC films, which may lead to some discrepancies between the two measurements.

3.3. Optical Stability of Mn-Doped MAPbBr₃ NCs

As discussed above, Mn²⁺ doping in MAPbBr₃ NCs enhances the PLQY by reducing non-radiative decay channels. Mn²⁺ doping also improves the long-term optical stability. Fig. 3 shows the PL stability of MAPbBr₃ NC films stored under ambient conditions over 180 hours. The as-synthesized xMn-MAPbBr₃ NCs exhibit PL intensity degradation, with the PL intensity retaining only 12% and 52% of the initial value for x = 0 and x = 0.17, respectively. This result indicates that Mn-doped perovskite NCs are significantly more stable than their undoped counterparts. To further enhance the optical stability, we treated the NCs with DDAB. After 180 hours under ambient conditions, the PL intensities of the DDAB treated NCs with x = 0 and x = 0.17 retained 62% and 72% of their original values, respectively, as shown in Fig. 3b. The DDA⁺ cations can replace the native oleic acid and oleylamine ligands on the NC surface or fill in missing ligands, thereby protecting the NCs from environmental factors such as humidity, oxidation, and other external degradation sources. Therefore, Mn²⁺ doping improves PLQY and the optical stability of MAPbBr₃ NCs by filling Pb²⁺ vacancies, passivating defects, reducing ion migration due to the stronger Mn–X bonds compared to Pb–X bonds, and enhancing the overall crystal robustness by minimizing lattice distortion.

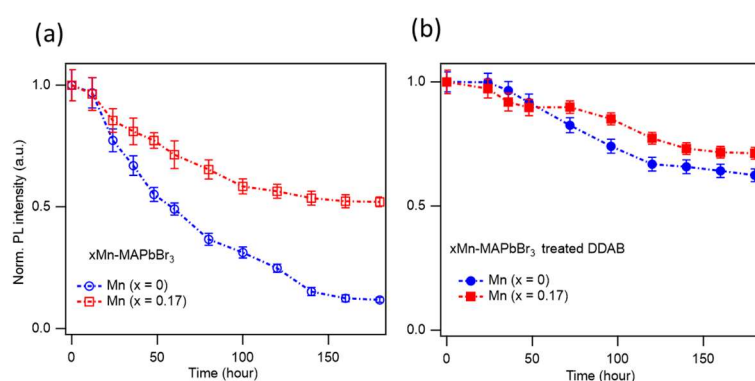


Figure 3. Optical stability of xMn-MAPbBr₃ samples with x = 0 and x = 0.17 over 180 hours for non-treat NCs (a) and for DDAB-treated NCs (b). The samples were diluted in toluene solvent and drop-cast on Si substrate for storage and measurement in ambient conditions.

3.4. Optical Properties at Low Temperature and Crystal Phase Transitions

Incorporating Mn²⁺ into MAPbBr₃ NCs may also affect the crystal structures, therefore affect crystallographic phases and phase transition temperatures. To investigate optical properties at different crystal phases, we perform PL spectra from 80 K to 280 K for two samples, non-doped and 17% Mn-doped NC. The latter case exhibits the highest PLQY for Mn-doped samples. Fig. 4 presents PL spectra, PL intensities, wavelengths, and linewidths of these two samples at different temperatures. Similar to previous observations in MHP NCs, the PL intensities decreased, the maximum PL peak blue shifted (emission energy increased), and the spectral linewidth broadened with increasing temperatures.^{63,64} Notably, the observed blue shift of PL with increasing temperature is opposite to the typical behavior seen in conventional semiconductors, where lattice expansion generally leads to a red shift. In conventional semiconductors, the valence band maxima (VBM) and conduction band minima (CBM) arise from bonding and antibonding orbital pair, respectively. As temperature increases, thermal expansion causes the crystal lattice to dilate, resulting in a reduction in bandgap energy, which can be described by the Varshni equation.⁶⁵ In contrast, the electronic structure of MAPbBr₃ crystals is fundamentally different. The VBM originates from a strong antibonding interaction between the Pb 6s and Br 4p orbitals, while the CBM arises from an antibonding combination of the Pb 6p and Br 4s orbitals.^{63,66,67} As the lattice expands with

temperature, the VBM shifts downward in energy due to its antibonding nature (weakened antibonding interactions between atoms), whereas the CBM is relatively insensitive to lattice deformation. This asymmetry leads to an overall increase in the bandgap with temperature. Both undoped and doped MAPbBr₃ NCs exhibit similar temperature-dependent behavior. However, an anomalous behavior is observed in Mn-doped MAPbBr₃ at around 220 K, where a sharp blue shift is followed by a red shift at 227 K. This irregular trend coincides with a threefold drop in PL intensity in the same temperature range (Fig. 4f). This suggests a possible phase transition occurring near 220 K. Further investigation is needed to clarify the origin of this unusual bandgap and PL intensity behavior in Mn-doped MAPbBr₃ NCs in this temperature range.

The linewidth (obtained from Gaussian fits to the PL spectra) broadening observed with temperature originates from enhanced exciton-phonon interaction, as more phonons participate in the emission process at higher temperatures. Although both acoustic and longitudinal optical (LO) photons can contribute to homogeneous PL linewidth broadening, LO phonons have been reported as the dominant factor in perovskite NCs.⁶⁴ The temperature-dependent linewidth broadening is nearly identical for both undoped and Mn-doped MAPbBr₃ NCs (Fig. 4 d).

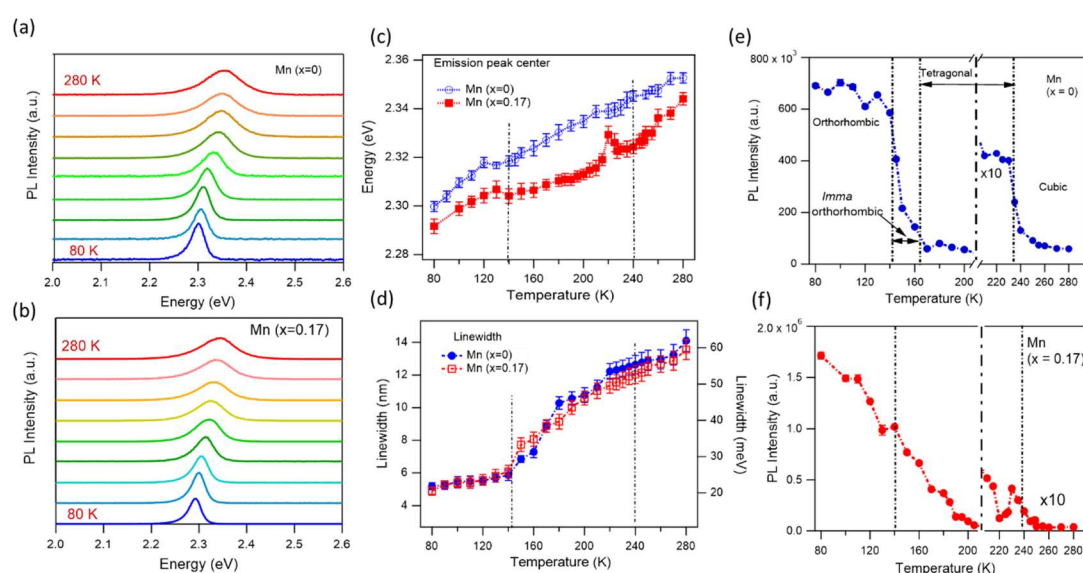


Figure 4. Temperature dependence of optical properties from 80 to 280 K. PL spectra of non-doped (a) and 17% Mn-doped (b) MAPbBr₃ NCs. (c) PL emission peak maxima in energy, (d) emission linewidths (obtained from Gaussian fits to the PL spectra), and (e-f) PL intensities for non-doped (blue) and 17% Mn-doped (red) NCs. Vertical dashed lines indicate the temperatures where the crystal phase transition happens. The dot-dashed line at 210 K in (e-f) represents where the data at temperatures > 210 K was magnified by 10x.

Figure 4 (e-f) presents the temperature-dependent PL intensities of the two samples. As the temperature increases, the PL intensities decrease due to enhanced NR recombination. At high temperatures, strong carrier-phonon interactions enable electrons or holes to acquire sufficient thermal energy to overcome potential barriers and transition into defect states, facilitating NR recombination. Conversely, at low temperatures, the MAPbBr₃ crystal structure becomes more ordered as the MA⁺ cations, which rotate freely at room temperature, are immobilized. This structural ordering can lead to higher emission rates and narrower spectral linewidths. Moreover, when temperature changes across the crystallographic phase transitions, the relative alignment between excited carriers and trap energy levels shifts. As a result, we expect abrupt changes in PL intensity due to variations in NR activation across the phase transition points. It has been reported that bulk MAPbBr₃ perovskites exhibit three distinct crystallographic phases: below 144 K is the orthorhombic (*Pnma*), between 144-237 K is the tetragonal phase (*I4/mcm*), and above 237 K is the cubic phase (*Pm3m*).⁶⁸ However, there has been debate regarding a transient phase within the 148–155 K range,

which has been attributed to phase coexistence.^{69,70} More recently, Abia *et al.* employed neutron diffraction to sequentially analyze the crystallographic phase at this temperature range and identified the phase as orthorhombic *Imma*.⁷¹ MAPbBr₃ perovskites in nanostructured forms, such as NCs, are suggested to suppress noticeable phase transitions, likely due to their reduced crystal size, which inhibits structural transformation. As a result, no clear PL intensity change is typically observed across the known phase transition temperatures.⁶⁴ We speculate that the absence of distinct PL intensity change in NCs across the phase transition points arises from effective surface passivation with high PLQY, which minimizes the influence of defects or traps across different crystal phases. To see crystal transition phases, we intended to keep the sample in ambient conditions for one week before measurements, starting from low PLQY (see Fig. 3). It is clear to see the phase transition temperatures for non-doped MAPbBr₃ NCs, Fig. 4e. During the orthorhombic-to-tetragonal phase transition, the PL intensity decreases by nearly 80-fold. Within the *Imma* orthorhombic phase (140-160K), the PL intensity gradually decreases. At the tetragonal-to-cubic transition (~135 K), the PL intensity drops by about fivefold. Within a single phase, the PL intensity remains relatively stable. In contrast, Mn-doped MAPbBr₃ NCs do not exhibit a clear orthorhombic-to-tetragonal phase transition. Instead, the PL intensity decreases steadily with increasing temperature. An anomalous change is observed at 220 K, accompanied by a corresponding shift in PL peak energy (see Fig. 4c). A sharp drop in PL intensity, approximately eightfold, occurs during the transition from the tetragonal to cubic phase. These results demonstrate that crystal phase transitions can be effectively tracked through temperature-dependent changes in PL intensity.

3.5. Superlattice Formation of *x*Mn-MAPbBr₃ NCs

NCs can self-assemble into highly ordered and periodic structures known as superlattices (SL). This artificial crystal-like arrangement facilitates inter-NC coupling, giving rise to emergent collective electronic, optical, or transport properties that are not present in uncoupled NCs. Most SLs reported to date have been formed using all-inorganic perovskite NCs, such as CsPbBr₃ synthesized via the hot-injection method, which yields high crystal quality and uniformity.⁷² The formation of high-quality superlattices relies heavily on the NCs' size and shape uniformity, as well as their surface chemistry. In contrast, hybrid organic-inorganic perovskites like MAPbBr₃, typically synthesized using the LARP method, often result in lower crystal quality and hence affect superlattice growth. However, as discussed above, Mn²⁺ doping in MAPbBr₃ has been shown to enhance NC quality, increase quantum yield, and improve material stability, factors that can promote the formation of higher-quality SLs. Furthermore, post-synthesis treatment with DDAB effectively passivates the NC surface, providing favorable conditions for self-assembly. In this study, we compared superlattice formation using pristine MAPbBr₃ NCs and Mn²⁺-doped MAPbBr₃ NCs (17% Mn²⁺), both treated with DDAB. Optical microscopy images (Fig. 5) reveal that Mn-doped NCs form well-defined SLs with a regular square shape, larger SL sizes (7–9 μm vs. 2–4 μm for the non-doped NCs), higher uniformity, and clearer backgrounds. Atomic force microscopy (AFM) shows SLs from pristine NCs have dimensions of ~3 μm in size and ~0.55 μm in thickness, whereas SLs from Mn-doped NCs reach ~8 μm in size and ~0.8 μm in thickness. Additionally, the surface of Mn-doped SLs is noticeably flatter. Two-photon fluorescence (2PF) imaging, performed using a femtosecond laser with 800 nm excitation, maps the PL distribution within the SLs (Fig. 5 g,h). Notably, 2PF intensities are higher localized at the edges of the Mn-doped SLs, which may indicate improved surface passivation at the edge surfaces.

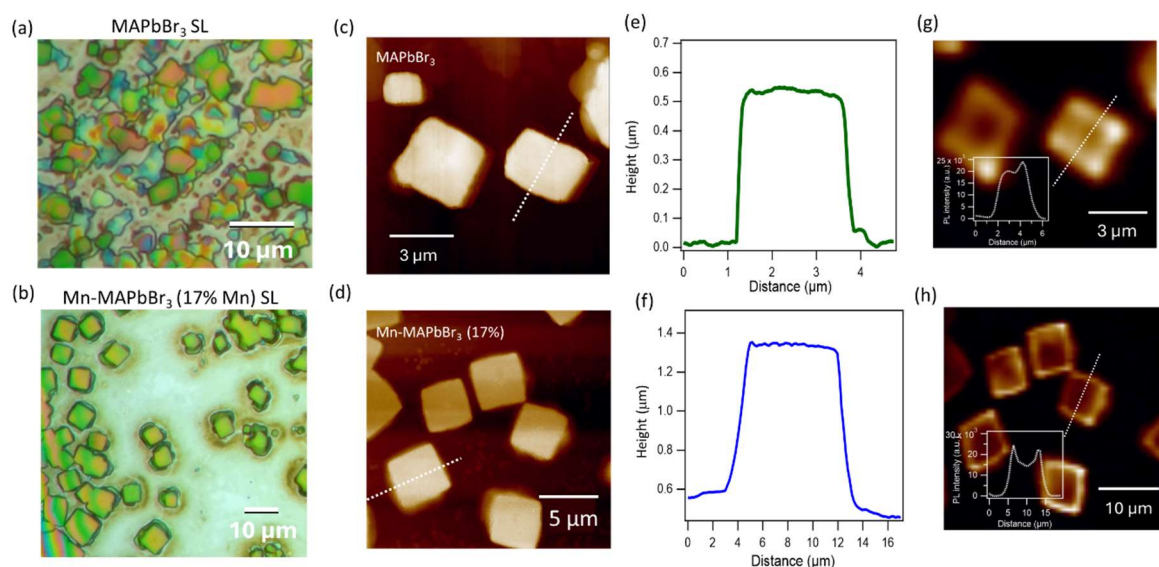


Figure 5. Superlattice characterization for non-doped (top row) and 17% Mn-doped (second row) MAPbBr₃ NCs. (a, b) Optical images of superlattices in the best area of SL formation, scale bar: 10 μm. (c, d) AFM images obtained using semi-contact mode. (e, f) AFM cross-sections obtained via the white dashed lines in (c-d). (g, h) PL confocal image obtained using two-photon fluorescence (2PF), the excitation laser is at 800 nm. Inset: the profiles of individual SL indicated by the white dashed lines.

4. Conclusions

In summary, we demonstrate that controlled Mn²⁺ doping in MAPbBr₃ NCs significantly enhances their optical performance and structural stability. Mn²⁺ ions are successfully incorporated into the perovskite lattice at concentrations up to 25%, inducing lattice contraction without compromising the crystal integrity or optical properties. This doping results in a notable increase in photoluminescence quantum yield, reaching a maximum of 72% at 17% Mn²⁺ doping, and a reduction in non-radiative recombination, as confirmed by PL dynamics and time-resolved measurements. Mn²⁺ doping also improves the ambient optical stability of the NCs, which is further enhanced by surface passivation using DDAB. Temperature-dependent PL studies reveal both conventional and anomalous emission behaviors in the Mn-doped samples. Structurally, Mn²⁺ doping enhances the robustness of MAPbBr₃ by filling vacancies and trap states and substituting Pb²⁺ sites without disrupting the lattice framework. Moreover, Mn²⁺ incorporation promotes the self-assembly of MAPbBr₃ NCs into superlattice structures, leading to larger nanocrystals and improved crystallinity. These findings offer valuable insights into the role of transition-metal doping in tuning the optical and structural properties of perovskite NCs, paving the way for the development of doped perovskites with improved functionality for lighting and optoelectronic applications.

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