Monitoring the Doping and Diffusion Characteristics of Mn Dopants in Cesium Lead Halide Perovskites

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ABSTRACT: Cesium lead perovskites, in the form of CsPbX₃ (X: Cl, Br, I) offer outstanding optical properties such as high photoluminescence quantum yield (PLQY) and defect tolerance and wavelength tunability. Moreover, these materials are solution-processable, and therefore, morphology and size can be easily controlled. Therefore, nanocubes, nanowire, nanoplatelets, or composition of NCs can be tailored. In this sense, either by adjusting the NCs size through morphology control or via anion-exchange reactions by adjusting the composition, one can cover the full visible spectrum or tune their optical properties. Cesium lead perovskites are potential candidates in a variety of optoelectronic and photonic applications such as solar cells, photodetectors, display, light-emitting diodes, and lasers.

Doping is a well-known strategy that may lead to novel functionalities and significant improvement in device efficiency. To date, various ions that are used as dopants for cesium halide perovskite crystals are investigated by performing experiments and first-principle calculations. First, it was observed that the presence of Mn ions causes a phase transition from Cs₄PbBr₆ to CsPbCl₃ during the doping process. Moreover, dopant-induced emission was found to decay exponentially over time due to diffusion of Mn atoms through the crystal surface. During the diffusion, apart from the optical degradation, structural changes, indicating the formation of Cs₄PbCl₆ phase, were also observed. At last, we performed density functional theory (DFT) and room-temperature molecular dynamics calculations to investigate the structural change and diffusion-driven optical phenomena.

INTRODUCTION

As a member of the colloidal semiconductor nanocrystal (NC) family, cesium lead halide perovskites in the form of CsPbX₃ (X: Cl, Br, I) offer outstanding optical properties such as high photoluminescence quantum yield (PLQY) and defect tolerance and wavelength tunability. Moreover, these materials are solution-processable, and therefore, morphology and size can be easily controlled. Therefore, nanocubes, nanowire, nanoplatelets, or composition of NCs can be tailored. In this sense, either by adjusting the NCs size through morphology control or via anion-exchange reactions by adjusting the composition, one can cover the full visible spectrum or tune their optical properties. Cesium lead perovskites are potential candidates in a variety of optoelectronic and photonic applications such as solar cells, photodetectors, display, light-emitting diodes, and lasers.

Doping is a well-known strategy that may lead to novel functionalities and significant improvement in device efficiency. To date, various ions that are used as dopants for cesium halide perovskite crystals have been reported. Among those, doping of cesium lead perovskites with Mn ions began to attract significant attention recently since the presence of Mn ions can add novel optical and magnetic features to NCs. For instance, Mn ions open an extra emission channel at ~590 nm due to transfer of exciton energy from host to d-states of Mn. In other words, dopant-induced emission is the result of radiative transition of electrons between host and the intragap states of dopant impurities. During this transition, energy is transferred from the electron–hole pair created via excessive energy of absorbed photon to the dopant levels, and as a result, dopant-induced emission occurs due to the electron–hole recombination taking place in the midgap states of dopant impurities. However, doping may create charge and size imbalance at the host lattice of these NCs that causes changes in both the crystal structure and the emission characteristics.

In this study, the effect of Mn ions on the structural and spectral properties of cesium lead halide perovskite crystals was investigated by performing experiments and first-principle calculations. First, it was observed that the presence of Mn ions causes a phase transition from Cs₄PbBr₆ to CsPbCl₃ during the doping process. Moreover, dopant-induced emission was found to decay exponentially over time due to diffusion of Mn atoms through the crystal surface. During the diffusion, apart from the optical degradation, structural changes, indicating the formation of Cs₄PbCl₆ phase, were also observed. At last, we performed density functional theory (DFT) and room-temperature molecular dynamics calculations to investigate the structural change and diffusion-driven optical phenomena.
degradation. As a result, this work presents a comprehensive view on the doping process, covering both the pre- and postdoping conditions.

**METHODOLOGY**

**Experimental Methodology, Materials.** Cesium bromide (CsBr, 99.9%, Sigma-Aldrich), lead(II) bromide (PbBr2 ≥ 98%, Sigma-Aldrich), manganese(II) chloride tetrahydrate (MnCl2·4H2O ≥ 98%, Sigma-Aldrich), oleic acid (OA, 90%, Alfa Aesar), oleylamine (OAm, 90%, Sigma-Aldrich), dimethylformamide (DMF, ≥ 99.9%, Tekkim), hexane (≥ 98%, Sigma-Aldrich), and toluene (≥ 99%, Merck) were purchased and used as received without any further purification.

**Synthesis of Undoped Cesium Lead Perovskite.** Following the synthesis method, 0.4 mmol of CsBr and 0.4 mmol of PbBr2 were dissolved in 10 mL of DMF, and then ligands OA (1.0 mL) and OAm (0.5 mL) were added to the solution under vigorous stirring. An aliquot of 0.5 mL from the prepared Cs+ and Pb2+ ions source was injected into 5 mL of toluene under vigorous stirring. The solution turned an explicit green color immediately, and after 3–4 min, it was centrifuged under 6000 rpm for 5 min. Precipitates were redispersed in hexane.

**Synthesis of Mn-Doped Cesium Lead Perovskite.** As Mn2+ source, MnCl2 (10 mmol) was dissolved in 10 mL of DMF. To obtain Mn-doped cesium lead perovskite, 0.5 mL of the Cs+ and Pb2+ ions source and 0.5 mL of the Mn source were injected into 5 mL of toluene under vigorous stirring. The solution became a bright green-yellow color rapidly, and after 3–4 min, it was centrifuged under 6000 rpm for 5 min. Precipitates were redispersed in hexane.

**Characterization.** The diffraction profiles of the cesium perovskites were recorded with an X-ray diffractometer (XRD, X’Pert Pro, Philips, Eindhoven, The Netherlands). Emission spectra were determined using an USB2000+ spectrometer (Ocean Optics Inc., Dunedin, FL) via a premium fiber cable. Raman (Horiba Xplora Plus) was used to determine fingerprint Raman-active vibrations of Cs+–perovskite structures.

**Computational Methodology.** Density functional theory-based calculations were performed using the projector augmented wave (PAW) potentials as implemented in the Vienna ab initio Simulation Package (VASP). The local density approximation (LDA) was used to describe the exchange and correlation potential. The Bader technique was solely employed. As reported previously, in addition to CsBrPb2Br6 there are also weak signals detected from small Cs4PbBr6 to CsPbCl3. According to the XRD data, it was found that its usage leads to significant modification in its structural, vibrational, and electronic properties (Figure 1).

**RESULTS**

**Mn Doping-Driven Structural Transition from Cs4PbBr6 to CsPbCl3 Phase.** Among those possible MnX2 (X: Cl−, Br−, and I−) precursors, MnCl2 was already reported as the one that favors the Mn incorporation most since the bond dissociation energy of the Mn–Cl is closer to the one of Pb–Cl compared the other possible Mn-X precursors and their corresponding Pb–X bonds. To achieve doping, MnCl2 was used during the synthesis of cesium lead perovskite crystals, and it was found that its usage leads to significant modification in its structural, vibrational, and electronic properties (Figure 1).

While the structural characteristics of the crystals are monitored by XRD and Raman spectroscopy, their electronic and optical properties are characterized via experimentally observed PL spectra and theoretically calculated band dispersions.

Figure 1a shows the reflection signals of both undoped and Mn-doped samples collected from X-ray diffraction. Apparently, diffraction pattern represented with a green line show that the Cs4PbBr6 phase forms first when the Cs+ and Pb2+ sources are solely employed. As reported previously, in addition to CsBrPb2Br6 there are also weak signals detected from small CsBrPb2Br6 crystals marked with *. However, the Mn-doped perovskite structure that shows orange color under UV light has sharp signals at 2θ: 15°, 22°, 31°, and 38° (black dashed lines). These intense XRD reflections not only indicate the formation of high crystalline Mn-doped perovskite material but also reveal the significant modification in crystal symmetry and structural transformation. Apparently, the XRD signals of the Mn-doped structure perfectly match with the tetragonal phase of CsPbCl3 represented with black dashed line (JCPDS 18-0366). Therefore, during the manganese-doping process that is done by using MnCl2 molecules, Br−→Cl halide exchange reaction also takes place. It is also seen that following the Br−→Cl exchange weak signals that belong to the CsPbBr6 become quite intense in the well-chlorinated crystal structure and Mn-doped sample contains no Cs4PbBr6 signals. On the other hand, signals marked with + correspond to excessive Mn ions that resulted in a trace amount of α-MnO2 (JCPDS 44-0141) along the sample. Therefore, it is clear from XRD spectra that adding MnCl2/DMF solution simultaneously with the Cs+ and Pb2+ ions source into toluene leads to a phase transformation from Cs4PbBr6 to CsPbCl3.
To monitor how the vibrational characteristics of the crystal evolve during the doping procedure, time-dependent room-
temperature Raman measurement was carried out using 785
nm laser excitation. As shown in Figure 1b, Raman peaks at 56,
68, 82, and 124 cm$^{-1}$ were obtained from the undoped sample,
indicating the formation of Cs$_4$PbBr$_6$ phase. On the other hand,
the Raman spectrum of the Mn-doped sample indicates that the
peak at 124 cm$^{-1}$ that originates from the Pb–Br phonon
modes in the [PbBr$_6$]$^{2-}$ octahedron vanishes; however
additional Raman shifts at 93, 153, and 190 cm$^{-1}$ appear.
Among these, while the peak at 93 cm$^{-1}$ corresponds to the
longitudinal optic (LO) mode of CsPbCl$_3$ crystal, the modes
at 153 and 190 cm$^{-1}$ stem from the Mn atoms. As a result,
Raman spectra also verify that using MnCl$_2$ together with Cs$^+$
and Pb$^{2+}$ ions source during the synthesis significantly modifies
the structure of resulting cesium lead perovskite phase.
Moreover, how the optical properties of the perovskite are
modified by Mn dopants was investigated by PL spectroscopy.
As shown in Figure 2a, there is a single narrow emission peak at
2.4 eV for the undoped structure. In this sense, emission at 2.4
eV originates from the CsPbBr$_3$ domains (their presence was
already verified in Figure 1a). However, as shown in Figure
2a, two prominent peaks were observed in the PL spectrum
after the Mn-doping procedure.

The ground-state electronic structures were also investigated
by performing density functional theory calculations. First,
cohesive energy calculations indicated that CsPbBr$_3$ and
CsPbCl$_3$ structures have cohesive energies of 3.37 and 3.67
eV/atom, and therefore, as long as there is a Cl-rich
environment, the formation of chlorine-exchanged domains is energetically more favorable. The calculated electronic band
structures of CsPbCl$_3$, CsPbBr$_3$, and Mn-doped CsPbCl$_3$ are
shown in Figure 2b. It is seen that while the halide exchange in
CsPbX$_3$ leads to ignorable modification in the electronic band
dispersion (band edges of both crystals lie at Γ point), the
CsPbCl$_3$ structure has wider bandgap than that of CsPbBr$_3$.
Thus, DFT calculations on the electronic structure, shown in
Figure 2b, showed that (i) the emission at 2.8 eV (443 nm) is
due to the CsPbCl$_3$ phase which has a direct bandgap at the Γ
high symmetry point and (ii) the presence of the Mn dopants
leads to midgap states at the vicinity of 2.1 eV (589 nm).

**Optical Stability of Mn-Doped CsPbCl$_3$.** To investigate
the optical stability of Mn-doped CsPbCl$_3$, its emission was tracked over time. As shown in Figure 3a, Mn-doped CsPbCl$_3$
casted on the glass slide emits orange color under UV
illumination (254 nm). It is seen from the photograph of the
UV-illuminated sample that the emission of Mn-doped
structure rapidly changes from orange to bluish color and
after 195 h under ambient conditions, perovskite completely
turned into blue.

To verify color change over time, the PL spectrum of the
orange perovskite crystal was registered at various times as
presented in Figure 3. It is seen that while the intensity of the
dopant-originated emission at 2.1 eV decreases rapidly, the
emission of the host crystal CsPbCl$_3$ at 2.8 eV remains almost
the same. Finally, the emission at 2.1 eV, that leads to the
orange coloring of the structure, completely disappears after
195 h. Here, the rapid decrease in the dopant-induced emission
over time is a kind of self-purification process that takes place via removal of dopant atoms from the crystal lattice through the
surface by diffusion. Moreover, the rate of change in the Mn-induced emission is shown in Figure 3c, indicating that the observed data well fits to the exponential decay equation
$y = y_0 + Ae^{-t/c}$, where $y_0 = 0.094$, $A = 0.884$, and $c = 54.219$. Apparently, the exponential
decrease of the peak stems from the diffusion of Mn atoms

![Figure 2](image2.png)

**Figure 2.** (a) PL spectra and (b) electronic band dispersion of undoped and Mn-doped samples.

![Figure 3](image3.png)

**Figure 3.** (a) Color change of the Mn-doped CsPbCl$_3$ perovskite under UV illumination (254 nm) in time. Photographs, from left to right, represent the Mn-doped CsPbCl$_3$ perovskite from its initial moment of casting (Mn-doped: initially) to 195 h later under ambient conditions. (b, c) Change of related PL spectrum and PL intensity of Mn-doped CsPbCl$_3$ perovskite under UV illumination (254 nm) in time, respectively. (d) Possible diffusion path of Mn atoms obtained from room-temperature molecular dynamics calculations.
from lattice to surface. At this point, for further theoretical examination of the possibility of diffusion of Mn atoms in the CsPbCl$_3$ crystal structure, ab initio molecular dynamics (MD) calculations were also performed. Constant temperature MD simulations for 10 ps duration time, as shown in Figure 3d, reveal that while the crystal structure remains stable at room temperature, Mn atoms can easily diffuse in the lattice sites by passing from the vicinity of Cs and Pb sites.

Modification in the crystal structure triggered by the diffusion of Mn atoms is also investigated by X-ray diffraction and Raman spectroscopy measurements at various times after casting the crystal dispersion from hexane. As shown in Figure 4a, additional reflection signals became visible after 96 h, indicating structural modification. The other XRD signals marked with # clearly indicate the reformation of the Cs$_4$PbX$_6$ (where X is Br or Cl) phase after Mn segregation. It is also seen that the XRD spectrum at 96 h includes some slightly blue-shifted 2θ values that resemble the undoped Cs$_4$PbBr$_6$ phase. However, the shift in signals is simply due to the Br$^-$Cl$^-$ exchange, which takes place during the addition of MnCl$_2$.

At the end of 195 h, an obvious broad background signal appears between 12 and 20°. This feature is called as amorphous halo. The occurrence of this signal after a long time duration may suggest the detachment of OA and OAm. Moreover, the number of XRD signals originates from the increase of the Cs$_4$PbCl$_6$ domain. On the other hand, the intensity of the α-MnO$_2$ characteristic signals (marked with +) increases over time. This increase can be explained by the growing population of MnO$_2$ at the crystal surface. It can be concluded that Mn-doped CsPbCl$_3$ crystals change their phase from Mn-doped tetragonal phase CsPbCl$_3$ to Cs$_4$PbCl$_6$ during the Mn-diffusion process.

Time-dependent room-temperature Raman measurements are also shown in Figure 4b. The prominent modes of Mn-doped sample at 92, 152, and 190 cm$^{-1}$ appear upon doping by Mn atoms. Mn-induced vibrational modes of the crystal, 152 and 190 cm$^{-1}$, were observed to vanish over time. After 195 h, two different regions were observed. In region A, which is presented with a navy blue line, the Raman shift became almost identical with the undoped one, but a few wavenumbers shifted due to halide exchange. In region B, presented with a turquoise line, a prominent peak occurs at 162 cm$^{-1}$, which is the indication of MnO$_2$.74

As a result, it is observed experimentally that there is a clear optical degradation of the Mn-induced emission at 2.1 eV over time, implying the diffusion of Mn atoms. Meanwhile, during the diffusion process, additional signals began to appear in both XRD and Raman measurements. Therefore, it can be concluded that the diffusion of Mn atoms leads to both optical and structural instabilities.

**Diffusion Dynamics at the Surface.** The diffusive motion of Mn atoms toward surface and the transition from CsPbCl$_3$ phase to Cs$_4$PbCl$_6$ were also investigated through first-principle calculations. As shown in Figure 5, two possible surface types, namely Cs- and Pb-terminated surfaces, were considered to investigate the absorption energy of Mn atom. The calculations reveal that the binding energy of the Mn atom on the Cs- and Pb-terminated surfaces of CsPbCl$_3$ are 4.74 and 5.19 eV, respectively. Bader charge analysis indicates that Mn atom donates 1.2e and 1.0e to Cs- and Pb-terminated surfaces, respectively. Therefore, considering the binding energy of Mn atoms inside the crystal structure, which is 1.24 eV at the most favorable lattice site, diffusive motion toward the surface is found to be inevitable.

On the other hand, the absorption energies of Mn atoms on the Cs- and Pb-terminated surfaces are significantly higher than the adsorption energies of OA and OAm, which are 698 and 463 meV for the Cs-terminated and 221 and 874 meV for the Pb-terminated surface, respectively.75 Therefore, the surface of the perovskite crystals, including either Cs- or Pb-terminated surfaces, prefer to bind Mn atoms by leaving the ligands. In such a case, expelled ligands then can bind to CsPbCl$_3$ surfaces that do not contain any Mn atoms and lead to ligand-mediated phase transformation from CsPbCl$_3$ to Cs$_4$PbCl$_6$. Among these ligands (OA and OAm), it was already reported that OAm by itself can trigger this process.76

Note that during the doping process, only some limited amount of the Mn (≤37%) can be doped into the CsPbCl$_3$ lattice as substitutional defects up to a 37% doping ratio were reported as achieved maximally when the synthesis method followed in this study was used.74 In any case, the crystals were found to be either Mn-doped (≤37%) or undoped (remain as...
neat host CsPbCl\textsubscript{3} crystals (≥63%), and the entire sample presents clear CsPbCl\textsubscript{3} characteristic signals together as given in Figure 1a. Compared to Mn-doped CsPbCl\textsubscript{3} crystals, neat host crystals show a more stable optical and structural response in time because both the host emission observed at 2.8 eV (Figure 3c) and characteristic signals of the CsPbCl\textsubscript{3} remain almost the same.

Neat CsPbCl\textsubscript{3} host crystals (not doped ones with ratio of ≥63%) were observed to be optically and structurally stable over time. On the other hand, Mn-doped perovskite crystals (≤37%) showed both optical and structural instabilities. The driver for these instabilities was investigated through theoretical calculations, and it was found that Mn ions diffuse toward the crystal surface resulting in both optical and structural instabilities.

**CONCLUSIONS**

In this study, the influence of Mn dopants on the structural, vibrational, and optical properties of Cs-perovskite crystals was investigated by performing experimental characterization tools and state-of-the-art first-principles calculations. It was found that the presence of Mn ions leads to a structural transition from the Cs\textsubscript{4}PbBr\textsubscript{6} to the CsPbCl\textsubscript{3} phase and opens an additional emission channel at ~2.1 eV. On the other hand, PL intensity of the dopant-induced emission was found to decay exponentially over time. DFT calculations revealed that the additional PL peak simply stems from the Mn-originated midgap states and the decaying behavior of emission is a consequence of diffusive motion of Mn dopants toward the crystal surface. Time-dependent XRD and Raman measurements also revealed that formation of MnO\textsubscript{2} at the surface and state-of-the-art computational resources were provided by TUBITAK ULAKBİM, High Performance and Grid Computing Center (TR-Grid e-Infrastructure). H.S. acknowledges computational resources were provided by TUBITAK under Project No. 117F095. The authors declare no competing financial interest.

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