Unlocking the Effect of Trivalent Metal Doping in All-inorganic CsPbBr₃ Perovskite

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ABSTRACT

Metal-ion doping is one of the most efficient approaches to precisely control the electronic and optical properties of perovskite nanocrystals (NCs). However, the origin of the dramatic contrast in the photoluminescence (PL) behavior of CsPbBr₃ NCs incorporating bismuth (Bi³⁺) and cerium (Ce³⁺) ion dopants remains unclear. Here, we demonstrate dominant PL quenching/enhancing centers both in the bulk and on the surface of Bi³⁺/Ce³⁺ doped CsPbBr₃ by calculating the dopant defect formation energies and charge-transition levels using high-level density functional theory (DFT). We show that the Bi³⁺ dopants introduce deep trap-states (antisite Bi_{Pb} and interstitial Bi_i) that are responsible for PL quenching. In sharp contrast, the Ce³⁺ dopants enhance the CsPbBr₃ lattice order and enrich the conduction band-edge states through antisite Ce_{Pb}, causing PL enhancement. Our findings not only provide new physical insights into the mechanism of the trivalent metal-ion doping effect, but also suggest a new strategy to control the dopant defect states for improving the optical performance of perovskite nanocrystals.

TOC GRAPHICS

Three-dimensional (3D) inorganic perovskite nanocrystals (NCs) have been considered as next-generation semiconducting materials for light-emitting diodes (LEDs), lasers, scintillators, and spintronic devices.¹⁻⁷ The potential industrial applications of 3D perovskite NCs are mainly due to their facile synthesis and attractive optoelectronic properties, such as narrow-band emission, tunable luminescence over the entire UV-visible-near IR spectral region, and high photoluminescence quantum yield (PLQY).⁸⁻¹² The most intensively investigated inorganic perovskites, CsPbX₃ (X = Cl⁻, Br⁻, or I⁻) NCs, exhibit remarkable PLQY,¹³ but synthesis strategies are needed to not only improve surface stability and charge carrier mobility but also to precisely engineer the electronic structure and interface for optoelectronic applications. For example, ligand modifications using short organic cations have been proposed as an effective way to passivate the surface uncoordinated Pb atoms² and introduce more halogen atoms to fill the vacancies.¹⁴ Metal-ion doping has also been considered as another promising avenue to control the electronic properties and optical performance of CsPbX₃ NCs.¹⁵⁻¹⁷

In the literature, a variety of dopants, including transition metals (Mn²⁺, Cu²⁺, Cd²⁺, Y²⁺)¹⁸⁻²², metalloids (Sn²⁺, Bi³⁺)²³, and lanthanides (Ce³⁺, Eu³⁺, Yb³⁺)²⁴⁻²⁶, have been incorporated to improve the optical properties of CsPbX₃ NCs due to the intrinsic ionic character and flexibility of the perovskite crystal structure. However, doping-related studies have rarely met the expectation that metal doping improves the photoluminescence efficiency of CsPbX₃ NCs, for reasons related to the quenching effects created by the appearance of trap states in the bandgap of the host CsPbX₃ NCs.¹⁶ For example, we reported that doping of Bi³⁺ ions into CsPbBr₃ perovskite nanocrystals (NCs) quenches the photoluminescence quantum yield from 78% to 8%.²³ Snaith and co-workers found that Bi³⁺-doped MAPbBr₃ single crystals (SCs) have increased electronic disorder and reduced carrier lifetime and PL intensity, which were attributed to the increase in nonradiative

recombination centers.²⁷ Based on these studies, Kanemitsu and co-workers showed that Bi^{3+} doping causes no significant changes in the band gap energy of MAPbBr_3 SCs but leads to an enhanced Urbach tail.²⁸ Miyasaka and co-workers have also demonstrated that the band gap of Bi -doped CsPbBr_3 SCs is comparable to their un-doped case; also, they found that Bi^{3+} doping causes no changes in the valence band structure, but an increase in the Fermi level of 0.6 eV is observed.²⁹ Hence, the decrease in PL intensity suggests that Bi^{3+} ions are incorporated into the CsPbBr_3 host lattice and create the bulk/surface trap states. In sharp contrast, Yao and co-workers incorporated lanthanide Ce^{3+} dopants into the CsPbBr_3 NCs lattice and achieved a significant enhancement in PLQY of up to 89% through increasing the dopant concentration.²⁴ In addition, Song and co-workers confirmed that Ce^{3+} ion-doped $\text{CsPbCl}_x\text{Br}_{3-x}$ NCs possess stable blue and green PL.³⁰

Here, we followed previously reported doping strategies with some modifications to obtain Bi^{3+} - and Ce^{3+} -doped CsPbBr_3 nanocrystals (NCs)²³⁻²⁴ and measured their steady-state absorption and PL spectra before and after metal-ion doping at the same dopant concentrations (see the details in the Experimental section of the Supporting Information). As shown in Figure S1, in the case of Bi^{3+} -doped CsPbBr_3 NCs, the first excitonic peak in the absorption spectra is very slightly shifted to higher energy, and the PL intensity gradually decreases with increasing Bi^{3+} dopant concentration. However, in the Ce^{3+} -doping case, the first excitonic peak exhibits a spectral blue shift as the dopant concentration increases, indicating effective incorporation of the metal ions inside the lattice, whereas the PL intensity is notably enhanced. This distinct PL behavior after Bi^{3+} and Ce^{3+} doping motivated us to uncover the underlying mechanism by which Bi^{3+} and Ce^{3+} ion doping affects the optical properties of CsPbBr_3 NCs using high-level density functional theory (DFT) calculations. Our results allow us to demonstrate how the dopants govern the electronic structures of CsPbBr_3 NCs and subsequently influence their optical properties. We also uncover

the mechanism for the dominant PL quenching and enhancing centers upon Bi^{3+} and Ce^{3+} doping, respectively, both in the bulk and on the surface of CsPbBr_3 NCs.

Figure 1. (a) Illustrations of the crystal structures of cubic- and orthorhombic-phase CsPbBr_3 with Bi^{3+} and Ce^{3+} dopants at Cs, Pb, and Br sites (Bi/Ce_{Cs} , Bi/Ce_{Pb} , and Bi/Ce_{Br}) and with Bi^{3+} and Ce^{3+} interstitials (Bi/Ce_i); (b) calculated doping formation energies; and (c) doping charge-transition levels for Bi/Ce_{Cs} , Bi/Ce_{Pb} , Bi/Ce_{Br} , and Bi/Ce_i in cubic- and orthorhombic-phase CsPbBr_3 calculated at the HSE+SOC level of theory.

To understand the Bi^{3+} and Ce^{3+} doping effects in the CsPbBr_3 bulk, we consider three different dopant antisites ($\text{Bi}/\text{Ce}_{\text{Cs}}$, $\text{Bi}/\text{Ce}_{\text{Pb}}$, and $\text{Bi}/\text{Ce}_{\text{Br}}$) as well as dopant interstitials ($\text{Bi}/\text{Ce}_{\text{i}}$), in both cubic and orthorhombic phases of CsPbBr_3 (see the illustrations in Figure 1a).^{1,31} Here, the dopant formation energies were calculated by considering the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional combined with spin-orbit coupling (SOC). The HSE+SOC method is an important tool to obtain accurate electronic structures of halide-lead perovskites containing heavy atoms as it corrects the underestimation of the band gaps evaluated at the PBE+SOC level³²⁻³⁴ (see more details in the *Computational Methods* of the Supporting Information; the thermodynamically stable region over which the dopant formation energies are calculated, is shown in Figure S2).

As shown in Figure 1b, for Bi^{3+} -doped CsPbBr_3 , both Bi_{Cs} and Bi_{Br} antisites have much larger formation energies than Bi_{Pb} , especially under Br-rich and moderate conditions, indicating that the Bi^{3+} ion preferentially occupies the Pb^{2+} ion position inside the CsPbBr_3 lattice as they have similar ionic radii (Pb^{2+} : 119 ppm vs. Bi^{3+} : 117 ppm) and metal-halide bond lengths (Pb-Br : 3.00 Å vs. Bi-Br : 2.93 Å). This finding agrees well with a previous theoretical study of Bi^{3+} -doped MAPbI_3 , which demonstrated that Bi_{Pb} is the dominant defect with a deep transition level.³⁵ Interestingly, interstitial Bi_{i} is also expected to form in the CsPbBr_3 host lattice due to its much lower formation energy under Br-poor conditions. This behavior suggests that interstitial Bi_{i} is mainly responsible for the experimentally observed Bi^{3+} ion emission in the near-infrared spectral range.³⁶

In the case of Ce^{3+} doping, Ce_{Pb} has also a much smaller formation energy than the other two antisites (less than 2 eV regardless of the growth condition), indicating that Ce^{3+} dopants can be incorporated to form Ce_{Pb} states with Ce-Br bond lengths of 2.93 Å in the bulk CsPbBr_3 lattice. The probability of forming interstitial Ce_{i} in CsPbBr_3 increases as we move from Br-rich to Br-poor conditions, and Ce_{i} becomes the dominant dopant defect in Br-poor conditions.

In addition, we find that Bi/Ce_{Pb} and Bi/Ce_{Br} have almost the same formation energies in the cubic and orthorhombic phases, whereas the Bi/Ce_{Cs} and Bi/Ce_i formation energies are larger for the cubic phase than the orthorhombic phase since the substitution of Cs⁺ with a dopant ion or the presence of an additional dopant ion would induce a larger change of the octahedral tilting angle in cubic-phase CsPbBr₃ compared to the orthorhombic phase. We also note that, while the dopant formation energies calculated at the GGA/PBE level (Figure S3) are larger than those obtained at the HSE+SOC level, the two sets of calculated energies have nearly identical evolutions as a function of growth condition.

The corresponding charge transition levels of these dopant defects are shown in Figure 1c. For Bi³⁺-doped CsPbBr₃, most of the considered dopant defects show deep transition levels within the bandgap in both cubic and orthorhombic phases: *i*) antisite Bi_{Pb} has a transition level energy located 0.59 eV below the conduction band minimum (CBM); and *ii*) interstitial Bi_i shows a deep transition level at ~0.7 below the CBM. The shallow transition level associated with Bi_{Br}(0/1+) and appearing at ~0.2 eV above the CBM is in fact difficult to generate due to its large formation energy. We recall that deep doping defect levels can act as carrier traps, leading to nonradiative recombination, whereas shallow levels can preserve the bulk electronic structure and do not degrade the optoelectronic properties.³⁷ Therefore, the dominant Bi_{Pb} and Bi_i that have the smaller formation energies could become nonradiative centers and capture the excited carriers from the host lattice.

In the Ce³⁺-doping case, however, the dominant dopant defects (Ce_{Pb} and Ce_i) have transition levels located 0.2 eV below the CBM and show shallow transition features in both phases. For both Bi³⁺- and Ce³⁺-doped CsPbBr₃, the other dopant-induced defects with deep transition levels about 0.3 eV below the CBM have very large formation energies and thus are not expected to

become effective nonradiative recombination channels. Our HSE+SOC calculations suggest that although the Bi^{3+} - and Ce^{3+} -doped CsPbBr_3 NCs have the same type of dominant dopant defects (*i.e.*, antisite $\text{Bi}/\text{Ce}_{\text{Pb}}$ and interstitial Bi/Ce_i), the photoluminescence properties of CsPbBr_3 NCs are determined by the specific charge transition levels of these dopants as well as the dopant density of states.

Figure 2. Projected density of states for the $\text{Bi}^{3+}/\text{Ce}^{3+}$ dopants at Pb^{2+} sites and $\text{Bi}^{3+}/\text{Ce}^{3+}$ interstitial sites in (a) $3 \times 3 \times 3$ cubic-phase and (b) $2 \times 2 \times 2$ orthorhombic-phase CsPbBr_3 supercells calculated at the HSE+SOC level of theory. The insets illustrate the electronic charge densities at the CBM after $\text{Bi}^{3+}/\text{Ce}^{3+}$ doping. The valence band maximum is set at zero energy.

Figure 2 shows the projected density of states (PDOS) for cubic-phase CsPbBr₃ after introducing the antisite Bi/Ce_{Pb} and interstitial Bi/Ce_i dopants, as calculated at the HSE+SOC level of theory. For pristine CsPbBr₃, the valence band maximum (VBM) and CBM of CsPbBr₃ are mainly composed of Br-4*p*, Pb-6*s*, and Pb-6*p* orbitals and show delocalized electronic distributions (see Figure S5 of the Supporting Information). In the case of Bi³⁺-doped CsPbBr₃, the appearance of Bi_{Pb} shifts the conduction band to lower energy (from 2.16 eV to 1.75 eV) once the Pb²⁺ ion is replaced by the Bi³⁺ dopant and shows a slightly delocalized charge density surrounding the Bi³⁺ ion at the CBM. Interstitial Bi³⁺ enriches the conduction band and introduces an additional state at the conduction band edge (located at ~2.1 eV) as well as a delocalized charge density at the CBM, as Bi³⁺ ions can be incorporated throughout the CsPbBr₃ lattice and lead to orbital hybridization between Bi-6*p* and Pb-6*p* orbitals. This is different from the PDOS of orthorhombic-phase CsPbBr₃ which shows a highly localized charge density at the CBM. The same conclusion can be drawn from the PDOS results obtained at the GGA/PBE level of theory (see Figure S6). Unlike the Bi³⁺-doped case, the band gaps of CsPbBr₃ in both phases remain almost unchanged after introducing the Ce³⁺ dopant at Pb²⁺ site, and the charge densities for CBM retain the delocalized feature. Moreover, the interstitial Ce³⁺ has a small contribution to the conduction band edge in the PDOS of cubic-phase CsPbBr₃, and the same electronic feature can be found in the orthorhombic case with an interstitial Ce³⁺. Overall, it can be concluded that the Bi³⁺ ion can significantly increase the number of defect states and the sub-bandgap density of states; on the other hand, Ce³⁺ can be doped into CsPbBr₃ NCs without introducing additional trap states and can slightly increase the electron density in the conduction band, which modulates the exciton relaxation and recombination of CsPbBr₃ NCs.

Figure 3. (a) Dopant formation energies for cubic and orthorhombic CsPbBr₃ when Bi³⁺ and Ce³⁺ dopants occupy surface Pb sites (Bi/Ce_{Pb}). (b) Surface energies for cubic- and orthorhombic- CsPbBr₃ slabs with surface Pb²⁺, Bi³⁺, and Ce³⁺. Projected densities of states for Bi³⁺/Ce³⁺ dopants at surface Pb²⁺ sites in (c) cubic- and (d) orthorhombic-phase CsPbBr₃ slabs, as calculated at the HSE+SOC level. The valence band maximum is set at zero energy. The insets show the electronic charge densities for the valence band minimum (VBM) and conduction band minimum (CBM) after Bi³⁺/Ce³⁺ surface doping.

Although dopants can be successfully incorporated into the bulk CsPbBr₃ lattice, these dopants are also anchored on the surface during the synthesis of CsPbBr₃ NCs, which can have a significant influence on the optical properties of doped NCs. To consider this scenario, we built slab models

where Bi^{3+} or Ce^{3+} ions occupy the Pb^{2+} sites and Br atoms are fully passivated at the top surface (*i.e.*, PbBr_2 surface) since the BiBr_3 and CeBr_3 precursors can bring extra Br atoms to passivate any uncoordinated Pb^{2+} atom. As shown in Figures 3a and 3b, we find: *i*) the formation energies of surface Bi_{Pb} assume negative values under moderate and Br-poor conditions and are even smaller than those of Bi_{Pb} in the bulk; *ii*) the surface Bi_{Pb} formation energies are much smaller than those of surface Ce_{Pb} ; and *iii*) the surface energies of the Bi^{3+} slabs are close to those of the pristine Pb^{2+} slabs, especially in the cubic phase.

These results indicate that Bi^{3+} dopants can be stabilized on the top surface of cubic-phase CsPbBr_3 compared to Ce^{3+} dopants. For the undoped slabs, both hole and electron distributions are delocalized along the whole slabs (see Figures S5c and S5d of the Supporting Information). Surface replacement with Bi^{3+} ion leads to the formation of a trap state below the conduction band, as well as a highly localized electron wavefunction on the top surface layers. Similarly to the bulk case, these localized states will act as nonradiative recombination centers for PL quenching. Therefore, although the surface treatment using BiBr_3 can provide extra Br atoms to passivate the uncoordinated Pb atoms on the surface, the surface Bi^{3+} dopant can still give rise to a significant number of nonradiative trap states and quench green emission. In sharp contrast, the surface replacement with Ce^{3+} dopant does not create any new in-gap trap states but instead slightly increases the density of states at the conduction band edge for both cubic and orthorhombic slabs. The deep trap states are also absent in the PDOS calculated at the GGA/PBE level (see Figures S6 and S7), and the band-edge dopant states appear more clearly. Such surface Ce^{3+} ions can stabilize the CsPbBr_3 surface and provide additional electronic states near the conduction band edge, thereby contributing to more emissive channels rather than nonradiative trapping centers.

Figure 4. (a) Normalized PL spectra of CsPbBr₃ NCs before and after Bi³⁺- and Ce³⁺-doping at different concentrations (2%, 5% and 10%, mole percentages). Schematic representation of the proposed doping mechanisms (Bi³⁺ and Ce³⁺ dopants at Pb sites and interstitials in the CsPbBr₃ bulk, and Bi³⁺ and Ce³⁺ dopants on the surface) and energetic diagrams depicting the PL quenching/enhancing process in (b) Bi³⁺-doped CsPbBr₃ and (c) Ce³⁺-doped CsPbBr₃.

According to the PL quenching/enhancing characteristics when using Bi³⁺ and Ce³⁺ dopants, as illustrated in Figure 4a, we propose the Bi³⁺- and Ce³⁺-doping mechanisms of CsPbBr₃ NCs depicted in Figures 4b and 4c. With excitation above the CsPbBr₃ bandgap, electrons are excited from the valence band into the conduction band of CsPbBr₃ NCs, followed by exciton formation, which can result in near-unity PLQY in such defect-tolerant NCs. However, solution-processed CsPbBr₃ NCs contain many defects, such as Pb²⁺ and Br⁻ vacancies. Both doping precursors (BiBr₃

and CeBr_3) play a dual role: *i*) dopant ions can occupy Pb vacancies in the bulk; and *ii*) additional Br^- atoms can fill Br^- vacancies in the bulk and terminate uncoordinated surface metal ions. By contrast, in the case of Bi^{3+} -doped CsPbBr_3 , due to the appearance of deep-trap energy levels associated with the dopant defects (Bi_{Pb} and Bi_i) in the bulk and on the surface of the CsPbBr_3 host, electrons in the conduction band can relax to the deep-trap state and then undergo nonradiative recombination. The photogenerated excitons can also transfer energy to Bi^{3+} ions with subsequent near-infrared emission. In the Ce^{3+} -doped case, Ce^{3+} ions can enhance lattice order through host relaxation when they are incorporated into CsPbBr_3 , and they do not create any deep trap states. Our unlocked doping mechanism can also be applied to understand the stability increment using isovalent small ions in hybrid perovskite³⁸ and PL enhancement using other lanthanide ions.²⁶

In summary, while there has been a large number of reports on the impact of metal-ion doping on the electronic and optical properties of perovskite materials, the mechanism underlying the occurrence of PL quenching in some instances and PL enhancement in others was not fully understood. Here, we have explored and rationalized the opposing effects of doping with the trivalent metals Bi^{3+} and Ce^{3+} on the electronic structure and PL properties of CsPbBr_3 NCs, using high-level DFT calculations. We have demonstrated that replacing Pb^{2+} with Bi^{3+} ions in the bulk or on the surface creates deep trap states that remove the defect-tolerant nature of the host CsPbBr_3 and function as nonradiative carrier recombination centers. Thus, these defect states act as trapping and scattering centers that significantly quench the PL intensity of the host NCs. By contrast, Ce^{3+} ions are able to stabilize the bulk/surface structure of CsPbBr_3 NCs and provide band-edge states leading to PL enhancement. Our findings highlight the importance and relevance of bulk/surface

dopant defects using trivalent metal ions for the optical performance of lead halide perovskites. These results are expected to generalize to other perovskite nanocrystals.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

Experimental and computational methods; crystal lattice parameters of investigated compounds; stability regions and represent active points; dopant defect formation energy and PDOS calculated at the GGA/PBE level.

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Notes

The authors declare no competing financial interests.

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