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Lanthanide-doped inorganic halide perovskites (CsPbX₃): novel properties and emerging applications

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Inorganic halide perovskites (IHPs) have provoked intense research efforts because of their superior stability, excellent optoelectronic properties, cost-effectiveness, and striking optoelectronic applications. Recently, the doping of lanthanide ions in IHPs has opened new avenues, particularly for emerging applications like NIR and white light-emitting diodes, NIR emitters, NIR cameras, optical temperature sensing, optical data encoding, etc. Besides, lanthanide doping has also significantly improved the stability (thermal, photo, and phase), structure and optical properties of IHPs, which has resulted in improved device performance. However, a comprehensive review of this development for IHPs is rare. This review article is an attempt to fill this gap and is designed to provide important fundamental aspects as well as recent developments in the field. It comprises all the basics, synthesis strategies, crystal structure (including phase transition and phase stability), and optical properties (absorption, emission, lifetime, quantum yield, exciton binding energy, and anisotropy) for pristine IHPs with special reference to CsPbX₃ (X = Cl, Br and I). The effects of lanthanide doping on the above-listed properties for IHPs are explored, and the doping of non-lanthanide metal ions such as alkali metals, alkaline earth metals, transition metals, and post-transition metals in all-IHPs are also covered for comparison. Furthermore, the review specifically outlines a few novel applications, which are due to the inherent merits of lanthanide doping in CsPbX₃. Potential challenges and future perspectives are also discussed.

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1. Introduction

Oxide perovskites are well known for their versatile applications in many fields, for example, in piezoelectricity, magnetism, superconductivity,^{1–4} *etc.* In the last two decades halide perovskites have shown a paradigm shift in the application of perovskites.^{5,6} Because of the direct bandgap, high absorption coefficient, high mobility, long carrier lifetime, cost-effectiveness, *etc.*, the all-inorganic cesium-lead halide perovskites (CsPbX_3 , where $\text{X} = \text{Cl}, \text{Br}, \text{and I}$) have been considered as rising stars for photovoltaic applications.^{7–11} They are also used in making colored and white LEDs,^{12–15} fluorescence sensors,¹⁶ oxygen detection sensors,¹⁷ gas sensors,¹⁸ humidity sensors,¹⁹ field-effect transistors,^{20,21} filter-free color image sensors,²² display applications,²³ photodetectors,^{24–26} spectro-chemical probes, explosive detectors,²⁷ laser fabrication,²⁸ X-ray detection,^{29,30} *etc.* In this review, we mainly discuss the basics of halide perovskites, including the major advantages and challenges of halide perovskites. Detailed structural and optoelectronic properties of inorganic halide perovskites (IHPs) are also discussed. The study of the doping effect of lanthanide ions in the IHPs and their novel and emerging applications are the focus of this review. To study the various optoelectronic properties of all inorganic halide perovskites (IHPs), CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$) has been chosen as a model system. Overall, the review article provides important fundamental aspects, as well as recent developments, in the field of IHPs.

Perovskites can be traced back to 1839 when a German scientist, Gustav Rose,³¹ encountered a new calcium titanate-based mineral in the Ural Mountain, on a journey to Russia. The mineral was then named “perovskite” in honor of the renowned Russian mineralogist Lev von Perovski. The materials with a similar structure to CaTiO_3 are known as perovskites. The general formula of perovskites is ABX_3 .³² In the ABX_3 structure, A occupies the corner position, B is at the body-centered position,

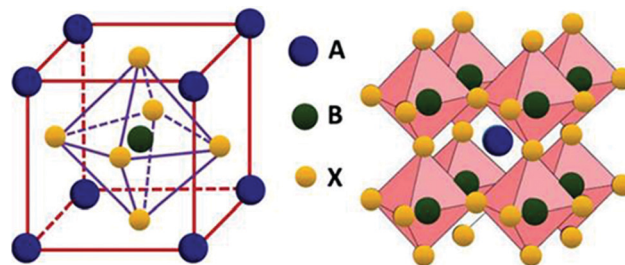


Fig. 1 Structure of perovskite with formula ABX_3 . Reprinted from ref. 32. Open access (2019).

and the face-centered positions are taken by the X atoms (see Fig. 1). The coordination number of B is 6, which is surrounded by the octahedral geometry formed by the X anions. The A atom has a coordination number 12 with cuboctahedral orientation. In general, the perovskites are characterized by the Goldschmidt tolerance factor, denoted as ‘ t ’, as follows:

$$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)}$$

where r_A , r_B and, r_X are the ionic radii of atoms A, B, and X, respectively.³³ To form the perovskite structure, the t value should be between 0.8 and 1.0. The t value between 0.9 and 1.0 for the perovskite structure likely forms a cubic structure, with an ideal cubic structure at $t = 1$. Whereas, in the range 0.8–0.89, a perovskite with a distorted crystal structure (*i.e.*, orthorhombic or tetragonal or rhombohedra) is formed. If t is less than 0.8, the size of the B-site cation is too large to form a perovskite structure, and an alternative structure such as ilmenite-type (*e.g.*, FeTiO_3) is formed. Similarly, for t greater than 1, the B cation is too small to achieve the desired t value and in this case, the hexagonal structure is formed.



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Table 1 Classification of perovskite materials

	Oxide perovskite A = inorganic cation B = inorganic cation X = oxygen SrTiO ₃ , ⁴⁰ GdScO ₃ , ⁴¹ BaTiO ₃ ⁴²		Organic–inorganic mixed halide perovskite (MA/FAPbCl _{3-x-y} Br _x I _y) A = organic cation B = inorganic cation X = two or more halide anions CH ₃ NH ₃ Pb(Br _x I _{1-x}) ₃ , ⁴³ CH ₃ NH ₃ PbCl _{0.5} Br _{2.5} ⁴⁴
Perovskite ABX ₃		Hybrid perovskite A = organic cation (MA ⁺ , FA ⁺) B = inorganic cation X = halide anions	
	Halide perovskite A = organic/inorganic cation (Cs ⁺ , MA ⁺ , FA ⁺) B = inorganic cation (Pb ²⁺) X = halide anions (Cl ⁻ , Br ⁻ , I ⁻)		Organic–inorganic halide perovskite (MA/FAPbX ₃) A = organic cation B = inorganic cation X = one halide anion HC(NH ₂) ₂ PbI ₃ , ⁴⁵ CH ₃ NH ₃ PbCl ₃ ⁴⁶ All-inorganic double perovskite (Cs ₂ B ¹⁺ B ³⁺ X ₆) A = inorganic cation B = two inorganic cations X = one halide anion Cs ₂ AgBiBr ₆ , ⁴⁷ Cs ₂ InAgCl ₆ ⁴⁸
		All-inorganic perovskite A = inorganic cation (Cs ⁺) B = inorganic cation X = halide anions	All-inorganic halide perovskite (CsPbX ₃) A = inorganic cation B = inorganic cation X = one halide anion CsPbCl ₃ , ⁴⁹ CsPbBr ₃ , ⁵⁰ CsPbI ₃ ⁵¹ All-inorganic mixed halide perovskite (CsPbCl _{3-x-y} Br _x I _y) A = inorganic cation B = inorganic cations X = two or more halide anions CsPbBr ₁ I ₂ , ⁵² CsPbCl _x Br _{3-x} ⁵³

In recent years, a class of perovskites with the general formula ABX₃, where A and B are cations and X is the halide, has attracted a great deal of interest. In halide perovskites, A site atoms are either organic [MA⁺: methylammonium (CH₃NH₃⁺), FA⁺: formamidinium (HC(NH₂)₂⁺)] or inorganic cations (Cs⁺), whereas B is the metal cation (Pb²⁺, Sn²⁺, Ge²⁺, *etc.*), and the X-site can have halides (Cl⁻, Br⁻, I⁻).^{34–36} When an organic cation (MA⁺, FA⁺, *etc.*) remains present at the A-site, it is called an organic–inorganic hybrid halide perovskite (*e.g.*, MAPbX₃, FAPbX₃).^{36–38} On the other hand, if an inorganic cation is present at the A-site, it is known as all-IHPs (for example, CsPbX₃).³⁹ The basic classes of perovskite structures, based on different types of atoms situated on A, B, and X sites, are listed in Table 1.

It is obvious from Table 1 that the halide perovskites are broadly classified into two categories, *i.e.*, hybrid (organic–inorganic) halide perovskites and all-IHPs. The first hybrid halide perovskite reported for visible-light harvesting was methylammonium lead iodide (CH₃NH₃PbI₃) in 2009.¹¹ It shows high efficiency in photovoltaic applications, however, it suffers from poor phase stability (particularly in a humid

atmosphere) and poor photo-stability.^{54,55} It was found that the all-IHPs show better stability under different environments, *e.g.* humid atmospheres, light illumination, electric field, high temperature, and electron beam, *etc.*⁵⁶ Li *et al.*¹⁰ carried out a comparative study of the stability of the hybrid halide perovskite and the all-IHPs in different atmospheres as listed in Table 2. The organic cations used in organic–inorganic halide perovskites, such as methylammonium and formamidinium, are among the major factors that result in phase instability.

Both the hybrid and the all-IHPs show bandgap tunability with changing the halide composition and through the variation of particle size, which eventually covers the entire visible spectral region (410–700 nm).^{57–59} However, the all-IHPs show strong excitonic and spin–orbital coupling effects, resulting in spin-selective excitonic transitions, providing a new field for spintronics and quantum-optics applications.^{59,60} Thus, researchers are intensively looking at all-inorganic metal halide perovskites, in which the organic cations of the hybrid perovskites are substituted with cesium ions, such as CsPbX₃ (X = Cl, Br, or I). The following sections in this review focus on the progress of CsPbX₃ perovskites and highlight the emerging applications.

Table 2 The stability comparison of hybrid and inorganic halide perovskites under different environmental conditions. Reproduced with permission from ref. 10. Copyright ©2020, Elsevier

Environment	Hybrid halide perovskite	Inorganic halide perovskite
Humid	(1) Degrades into HI, PbI ₂ , and volatile organics	(1) Induces a phase transition and reversibly transforms into its initial phase by heating to 350 °C under humid conditions
Illumination	(1) Decomposes into PbI ₂ , metal lead, molecular iodine, and other volatile products (2) Superoxide reacts with the protonated MA ⁺ and further decomposes its structure	(1) Superior thermal and photochemical stability (2) Acid protons are absent in Cs ⁺ ions and make their structure more stable
Electric field	(1) Migration barrier is lower under illumination (2) Rapidly and irreversibly decomposes to PbI ₂ under humid conditions	(1) Migration barrier is higher under illumination
High temperature	(1) The loss of organic components; perovskite degrades into PbI ₂	(1) Phase transition in four different phases
Electron-beam	(1) Defect formation due to irradiation damage, and phase transformation induced by electron-beam heating (2) Decomposes under the electron beam	(1) Remain stable and does not degrade under the electron beam (2) The intensity of the excitonic peak remains stable without the appearance of any high-energy peaks

2. All-inorganic halide perovskite CsPbX₃ (X = Cl, Br, or I)

2.1 Synthesis methods of CsPbX₃

There are various methods for synthesizing bulk and nanostructured all-IHPs. Nasstrom *et al.*⁶¹ prepared CsPb(Br_xI_{1-x})₃ film, taking x between $x = 0$ and $x = 2/3$, using an inkjet printing technique, and $x = 0.85$ and $x = 1$ by spin coating. In another study, the efficient CsPbBr₃ perovskite film was developed for solar cell applications by using a single-crucible vacuum thermal evaporation method.⁶² Recently, Borri *et al.*⁶³ reported the synthesis of CsPbBr₃ film of about 70 nm thickness by using RF-magnetron sputtering techniques on the glass substrate. In this method, the CsPbBr₃ powder, prepared by mechanochemistry, is pressed for 24 hours by a pneumatic press (working pressure 11.5 MPa) and sputtering deposition was carried out at room temperature. The RF power of 20 W was maintained in an argon environment with a flow rate of 20 atm cm³ min⁻¹. This is one of the powerful techniques for thin-film deposition, both for conductive and non-conductive materials, and may attract researchers in the future. Zhang *et al.*⁶⁴ synthesized CsPbBr_{1.2}I_{1.8} nanocrystals (NCs) using the hot injection method. The colloidal solution of CsPbBr_{1.2}I_{1.8} NCs was spin-coated at room temperature on a fused silica substrate. This formed a solid film and was used to study the light-induced phase segregations and optical studies. Liu *et al.*⁶⁵ used modified hot injection techniques to synthesize all-IHPs quantum dots (QDs). In this technique, the organolead compound trioctylphosphine-PbI₂ was swiftly injected into a 1-octadecene (ODE) solution, heated to 100–170 °C, which contained oleic acid (OA), oleylamine (OAm), and Cs-oleate.

All these methods have certain advantages and disadvantages. One common challenge observed in all the methods discussed above is poor long-term stability against moisture. However, the film deposited using the thermal evaporation method showed comparatively longer film stability.⁶⁶ The hot injection method, because of the requirements of high temperature and inert conditions, is neither cost-effective nor industrially viable.¹⁵ However, it shows high thermal stability

and distinct optical features.⁵⁷ The single-crucible vacuum thermal evaporation techniques used by Li *et al.*⁶² have advantages over multi-crucible vacuum thermal evaporation techniques. In multi-source (crucible) thermal techniques, the evaporation rate of the source material is highly dependent on parameters like the pressure of the vacuum chamber, the quality of evaporation materials, and the heating rate of the crucible. During the whole synthesis process, the adjustment of all these parameters for controlled evaporation is a difficult task so the single-crucible method is the best alternative to a multi-crucible method.

Thin-film deposition using the RF sputtering technique is suitable for both conductive and nonconductive materials.⁶³ It also provides uniform thin-film limited contamination and ease of doping. The major challenge of this technique is the controlled monitoring of parameters like pressure, deposition rate, and RF power to get a uniform thin film. In the modified hot injection method used by Liu *et al.*,⁶⁵ the particle size can be easily tuned by the injection temperature. In the modified hot-injection method, the organolead compound trioctylphosphine-PbI₂ (TOP-PbI₂) is taken as the reacting precursor. Fig. 2 shows a comparative study of conventional hot injection and modified hot injection methods based on Stokes shifts and PLQYs. The all-IHPs prepared by conventional methods show noticeable Stokes shifts that also vary with the particle size. However, the modified hot injection method shows almost constant Stokes shifts for the different sizes of QDs indicated in Fig. 2(a). The absorption coefficient of TOP-CsPbI₃ QDs is higher than conventional OA/m-based CsPbI₃ QDs as shown in Fig. 2(b). The photoluminescence quantum yields (PLQYs) are stable for different sizes of QDs in the modified method.

The phosphine ligand-modified hot injection method was also reported by Li *et al.*⁶⁷ to improve the emission intensity and stability of CsPbBr₃ QDs under different atmospheres. The trioctylphosphine (TOP), tributylphosphine (TBP) and diphenylphosphine (DPP)-modified CsPbBr₃ QDs show high PL intensity and improved stability as compared to CsPbBr₃ QDs in ethanol, water and UV light irradiation. This may be attributed to the steric effect of the multi-branched phosphine ligand.

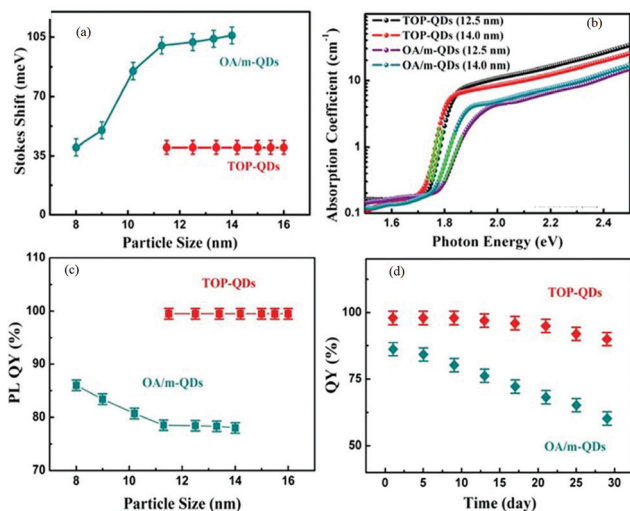


Fig. 2 (a) Stokes shift of the TOP-QDs and OA/m-CsPbI₃ QDs as a function of their particle sizes. (b) Optical absorption spectra of different sized TOP-QD and OA/m-CsPbI₃. (c) PLQYs of OA/m-QDs and TOP-QDs as a function of their particle sizes. (d) Change in the PLQY of the OA/m-QDs, TOP-QDs versus storage duration. QD solutions synthesized at 140 °C were stored in a sealed bottle under ambient conditions. Before the QY measurement, all QD samples were washed twice using MeOAc. Reproduced with permission from ref. 65. Copyright©2017, American Chemical Society.

2.2 Phase and phase transitions of CsPbX₃

Structure–property correlation makes it important to know about various phase transitions in halide perovskites. It affects the phase stability and the performance of devices like photovoltaic cells, light-emitting diodes, *etc.* The perovskite structure shows a stable cubic structure at high temperatures that switches to distorted metastable tetragonal and orthorhombic phases at low temperatures. The phase transition temperature depends on the perovskite composition and also to a lesser extent on sample preparation techniques. The formation enthalpy of different phases in the halide perovskite can be computed using the DFT method (even for the same composition) as follows:⁶⁸

$$\Delta H_{\text{ABX}_3} = E_{\text{ABX}_3} - \mu_{\text{A}} - \mu_{\text{B}} - 3\mu_{\text{X}} \quad (1)$$

where E_{ABX_3} is the DFT calculated total energy, and μ_{A} , μ_{B} , and μ_{X} are the chemical potentials of the A, B, and X elements, respectively. In the perovskites, the lower symmetry structure has a more favorable formation enthalpy than the cubic structure. The orthorhombic structure $Pnma$ phase has a lower formation energy and is the most commonly formed perovskite structure. The phase transitions in CsPbX₃ (X = Cl, Br, or I) are explained individually in Sections 2.2.1–2.2.3.

2.2.1 Phase transitions in CsPbCl₃. The phase transition in CsPbCl₃ has been studied by various groups using different methods such as neutron-scattering,⁶⁹ nuclear magnetic resonance,⁷⁰ differential thermal analysis (DTA),⁷¹ temperature-dependent linear expansion and birefringence curves,⁷² and differential scanning calorimetry (DSC),⁷³ *etc.* In CsPbCl₃, neutron-scattering and differential thermal analysis-based results suggest that the phase transition from the cubic to the

tetragonal phase occurs at 320 K, tetragonal to an orthorhombic phase at 315 K, and finally orthorhombic to the monoclinic phase at 310 K.^{69,71} The DTA shows two anomalies, namely, an effectively larger one at 320 K and a relatively smaller one at 315 K, which are the consequences of the phase transition from the cubic to the tetragonal phase and the tetragonal to orthorhombic phase, respectively.⁷¹ The temperature-dependent linear expansion and birefringence curves of CsPbCl₃ single-crystals also indicate sudden changes in the curves at about 310 K, 315 K, and 320 K.⁷² These are clear evidence of phase transitions in the CsPbCl₃ single crystal. The phase transition in CsPbCl₃ has also been confirmed by the DSC technique.⁷³ A sharp peak was observed at 321 K and a small peak at about 316 K in a specific heat change vs. temperature graph, in good agreement with the phase transition temperature observed from other techniques.

2.2.2 Phase transitions in CsPbBr₃. For the study of phase transitions in CsPbBr₃, several methods, such as selected area electron diffraction (SAED),⁷⁴ neutron diffraction,⁷⁵ high-temperature X-ray diffraction,^{76,77} and DSC,^{76–78} have been used. Zhang *et al.*⁷⁴ studied phase transition in single-crystal CsPbBr₃ (synthesized using inverse temperature crystallization method) using the SAED patterns monitored through transmission electron microscopy (TEM) at various temperatures. The SAED patterns at different temperatures are shown in Fig. 3. The room temperature SAED pattern was characterized as the $Pbnm$ space group of orthorhombic cells. On increasing the temperature, the phase transition from the orthorhombic to $P4/mbm$ tetragonal structure was observed at 90 °C. Upon further increasing the temperature to 133 °C the transition from the tetragonal to the cubic structure was observed. However, CsPbBr₃ perovskite synthesized using the hot injection method showed an orthorhombic phase below 130 °C.¹⁵ At temperatures above 130 °C, it showed a cubic phase that retained the same structure up to 200 °C. Rodova *et al.*⁷⁷ also studied the phase transition of CsPbBr₃ using high-temperature X-ray diffraction and DSC. At room temperature, it showed the orthorhombic structure ($a = 8.207 \text{ \AA}$, $b = 8.255 \text{ \AA}$, and $c = 11.759 \text{ \AA}$, $Pbnm$ space group). The phase transitions from orthorhombic to tetragonal ($a = 8.259 \text{ \AA}$, $b = 5.897 \text{ \AA}$; $P4/mbm$ space group) and tetragonal to cubic ($a = 5.874 \text{ \AA}$, $Pm\bar{3}m$ space group) were observed at 88 °C, and 130 °C, respectively. The neutron diffraction study carried out by Hirotsu *et al.*⁷⁵ also indicated the transition temperature from the cubic to tetragonal phase and tetragonal to orthorhombic phase at 130 K and 88 K, respectively. Thus, the synthesis technique and synthesis temperature both affect the phase transition in CsPbBr₃.

2.2.3 Phase transitions in CsPbI₃. Marronnier *et al.*⁷⁹ studied the phase transitions in CsPbI₃ halide perovskite and observed four different phases. Three of them have the perovskite structure α - $Pm\bar{3}m$ (cubic), β - $P4/mbm$ (tetragonal), and γ - $Pbnm$ (orthorhombic) and the fourth one δ - $Pnma$ is a non-perovskite structure. The three perovskite phases of CsPbI₃, namely, the α , β , and γ -phases, are also called “black phases” and the non-perovskite δ -phase is called the “yellow phase”.^{80,81}

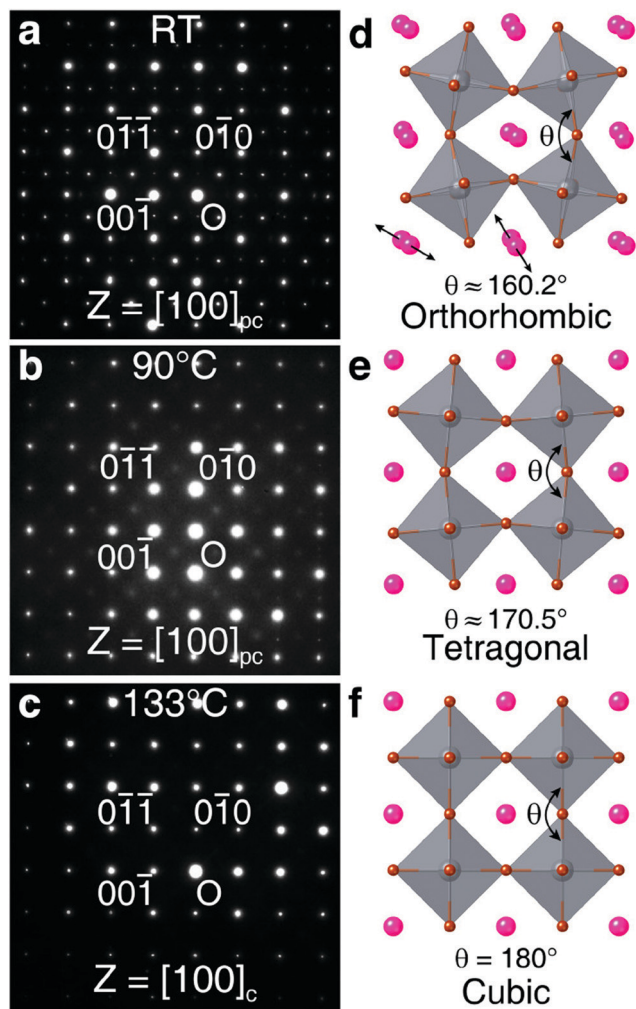


Fig. 3 The SAED patterns obtained for the CsPbBr₃ single-crystal at (a) room temperature, (b) 90 °C, and (c) 133 °C. (d–f) The orthorhombic, tetragonal, and cubic structures, respectively, for CsPbBr₃. Reproduced with permission from ref. 74. Copyright©2020, American Chemical Society.

Fig. 4 shows the crystal structures of all these phases. It was observed that on increasing the temperature, a direct phase transition from the non-perovskite δ -*Pnma* to the perovskite cubic *Pm* $\bar{3}$ *m* phase occurred at 595 K.⁷⁹ This is a stable phase at high temperature. While cooling down, all the four crystal structures, cubic, tetragonal, orthorhombic, and non-perovskite, were observed. In the cooling process, the phase transition from the cubic perovskite structure α -*Pm* $\bar{3}$ *m* phase to the tetragonal structure β -*P4*/*mbm* occurred at 539 K, the β -*P4*/*mbm* to orthorhombic structure γ -*Pbnm* was observed at 425 K and finally, the transition to the non-perovskite structure δ -*Pnma* phase occurred at room temperature. The bandgap of the non-perovskite yellow δ -*Pnma* phase was 3.01 eV and was stable at room temperature. The γ -phase orthorhombic structure was more stable under ambient conditions.^{82,83}

A comparative study of the phase transition in CsPbX₃ indicates that the transition from the cubic structure to the tetragonal in CsPbCl₃, CsPbBr₃, and CsPbI₃ takes place at

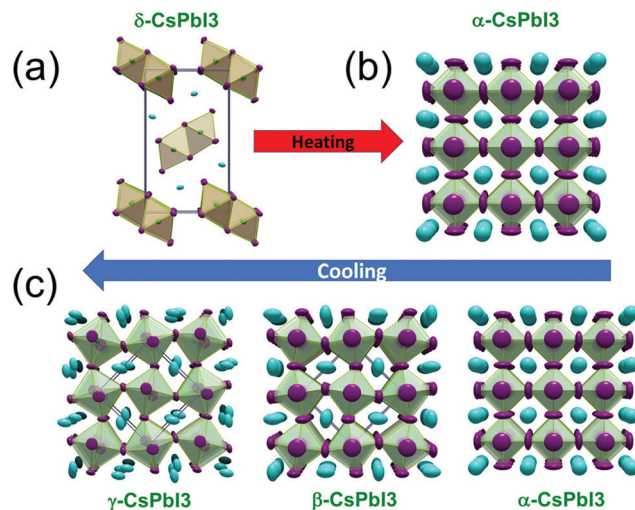


Fig. 4 The phase transitions in CsPbI₃: (a) the initial yellow non-perovskite δ -phase directly converts to (b) the black perovskite α -phase as the temperature exceeds the transition temperature on heating. (c) Upon cooling, the black perovskite α -phase undergoes various phase changes, namely, the tetragonal structure β -phase, orthorhombic structure γ -phase. These phases are metastable and finally transform into the thermodynamically stable δ -phase upon standing. Reproduced with permission from ref. 79. Copyright©2018, American Chemical Society.

320 K, 406 K, and 595 K, respectively.⁶⁸ The greater the size of the halide ion, the higher is the transition temperature. These transitions produce structural distortions in the crystal. The phase transition-induced structural distortions can be divided into three categories: (i) polar displacement of the A or B cations away from their high symmetry positions, (ii) rigid tilting of the corner-sharing BX₆ octahedra, and (iii) the collective Jahn–Teller distortion of the BX₆ octahedra.⁶⁸ The corner-sharing BX₆ octahedra tilting is associated with the size of the A-site cation and the ratio of the cavity volume to the A-site cation size. The smaller size A cation affects the Goldsmith's tolerance factor (*t*) and leads to a distortion in the network. Similarly, the larger the volume of the octahedral cavity to the size of the A-site cation ratio, the greater the tilting of the octahedra.

2.3 Stability of CsPbX₃

The stability of halides is one of the major concerns that can be changed by modifying its internal structure; *i.e.*, A and B-site cations, halide compositions, size reduction, and surface modification. As discussed, ions at A, B, and X-sites in the ABX₃ halide perovskite affects the value of the Goldsmith tolerance factor "*t*", and the octahedral factor ($\mu = r_B/r_X$), which determines the structure formed. The value of *t* between 0.8 to 0.9 forms the distorted perovskite tetragonal or orthorhombic structure, and between 0.9 to 1.0 most likely forms a cubic structure with the most stable α -phase cubic structure at *t* = 1.^{21,84,85} According to the definition of *t*, the larger A-site cations favor higher *t*-values that make the halide perovskite structure more stable.^{21,84} Cs⁺ is almost the largest inorganic cation in the periodic table. Therefore, we cannot find a better

choice for its replacement in the periodic table for the synthesis of all-IHPs. Consequently, researchers have incorporated some organic cations into the CsPbX_3 but it produces a negative effect on the stability of the structure. The t -value greater than 1.0 implies that the size of the B atom is too small or the X atom is too large. Similarly, for t -value less than 0.8, the size of the B atom is too large or the X atom is too small to form a perovskite structure. These conditions lead to the formation of a non-perovskite structure.⁸⁶ In the ABX_3 perovskite structure, the B atom remains situated at the center of the octahedra formed by B and X atoms. The octahedral factor " μ " has an important role in octahedral stability. For the perovskite structure, the μ value should be $0.414 < \mu < 0.732$.⁸⁵ It plays a significant role in determining the size of the $[\text{BX}_6]^{4-}$ octahedral and the cuboctahedral voids. Thus, the factor t and the factor μ are interconnected for the structural determination in all-IHPs. Hence, the substitution of smaller sized cations at the B-site decreases the size of the octahedra and thus increases the t value, which results in an increased stability.⁸⁶ It has been reported that at room temperature, the stability of the halide perovskite increases from X = I to Br to Cl; *i.e.*, for smaller X-site ions.⁸⁷ All these halide perovskites are stable at the higher temperatures. The low stability of CsPbI_3 at low temperature is because of the tilting of the $[\text{PbI}_6]^{4-}$ octahedra, where the size of the cuboctahedral void available for the A-site atom is much larger than the Cs^+ atom.

The stability of all-IHPs is improved to some extent by the use of various organic surface-capping agents. Therefore, different organic compounds have been widely used to stabilize the perovskite structure.⁸⁸ In the synthesis of CsPbX_3 using the hot injection method, the Cs-oleate is injected *in situ* at elevated

temperature into octadecene (ODE) solution containing PbI_2 , oleic acid (OA), and oleylamine (OAm). The particles are stabilized with both long-chain carboxylic and oleylammonium surface ligands.⁶⁵ In CsPbI_3 QDs, the ammonium ligands are easily lost because of the weak acid-base interactions arising between the I^- and oleylammonium during the essential purification procedures, resulting in a fast agglomeration and consequently a phase transformation from the α -cubic phase to a non-perovskite δ -phase.

The stability of the halide perovskite under a humid atmosphere and at elevated temperatures is of great concern. This can be increased by the surface modification by complex layers such as moisture-resistant layer(s), encapsulation, passivation, or by the use of additives.⁸⁹ Phenylethylammonium chloride (PEACL), *p*-phenylenediammonium iodide (PPDI), and phenylethylammonium iodide (PEAI) have been widely used to address these concerns. They also improve the hydrophobic properties of all-IHPs and thereby stabilize the black phase perovskite structure. The hydrophobic alkyl chain or the conjugated heterocycle contained in the organic cations are believed to increase the humidity resistance.⁹⁰ The XRD patterns of CsPbBrI_2 and CsPbBrI_2 -PEI thin films under different environmental conditions are shown in Fig. 5(a-c). The XRD pattern of the CsPbBrI_2 -PEI thin film remains unaffected under $80 \pm 5\%$ relative humidity (RH) for 0.5 h and under heating up to 85°C in an N_2 glove box for 72 h. Whereas, the CsPbBrI_2 treated under the same environmental conditions reflects significant changes in the intensity of XRD peaks, as well as the evolution of random peaks in the XRD pattern, which indicate poor stability under these environments. The significant improvements in the PL intensity for CsPbBrI_2 -PEI was

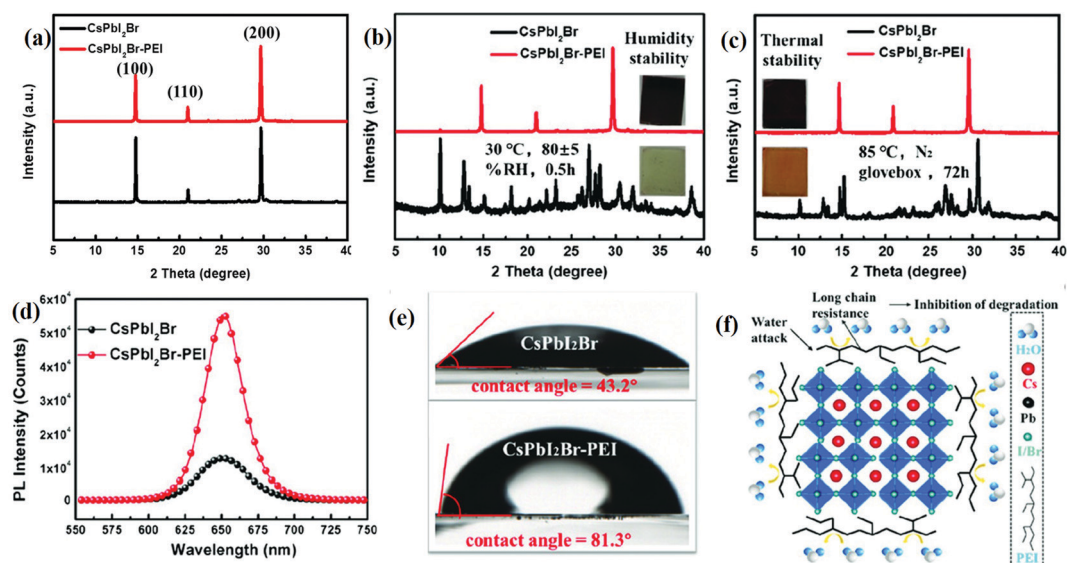


Fig. 5 The XRD spectra of the (a) CsPbI_2Br and $\text{CsPbI}_2\text{Br-PEI}$ thin-films. (b) CsPbI_2Br and $\text{CsPbI}_2\text{Br-PEI}$ films after being exposed to $80 \pm 5\%$ RH for 0.5 h (the inset shows images of samples after being exposed to $80 \pm 5\%$ RH for 0.5 h). (c) CsPbI_2Br and $\text{CsPbI}_2\text{Br-PEI}$ films heated at 85°C in an N_2 glovebox for 72 h (the inset shows images of samples after heating at 85°C in an N_2 glovebox for 72 h). (d) PL spectra of the CsPbI_2Br and $\text{CsPbI}_2\text{Br-PEI}$ thin films. (e) The water contact angles of CsPbI_2Br film and $\text{CsPbI}_2\text{Br-PEI}$ film. (f) A schematic diagram of the long-chain wrapping of CsPbI_2Br grains. Reproduced with permission from ref. 90. Copyright©2020, Wiley Online Library.

also observed as indicated in Fig. 5(d). The CsPbBr₂-PEI demonstrated hydrophobic behavior due to the long alkyl chain present at the grain boundaries, as shown in Fig. 5(f). The extent of hydrophobic character was measured by the contact angle and was 81.3° for CsPbBr₂-PEI, and 43.2° for CsPbBr₂. The XRD pattern of the CsPbBr₂ film was completely transformed into the yellow phase under the relative humidity of 85% for 30 min but the CsPbBr₂-PEI pattern remained unchanged, which confirmed the hydrophobicity characteristics as indicated in Fig. 5(e).⁹⁰ The CsPbBr₂ film suffered phase transition from the α -phase (black color) to the δ -phase (reddish-brown color) due to thermal degradation in the N₂ environment. PEI effectively stabilized the CsPbBr₂-PEI film during the annealing process and the α -phase was retained at this temperature as shown in Fig. 5(a-c).⁹⁰ The van der Waals forces among the PEI alkyl chains increased the crystal formation energy which resulted in enhanced phase stability. Polyethyleneimine (PEI) was used to reduce the defects in the all-IHPs, and it increased the phase as well as the structural stability of the CsPbBr₂ perovskite against humidity and temperature.

Zhang *et al.*⁹¹ used *n*-butylammonium iodide (BAI) in CsPbBr₂I to improve factors like the crystallization and morphology of the structure. The BAI incorporation decreases the trap state density and nonradiative recombination and thereby facilitates preparation at the reduced annealing temperature. An aromatic bi-functional ligand *L*-phenylalanine (*L*-PHE) in the *in situ* management of the present surface ligand environment stabilizes the phase of CsPbI₃ by coordinating with the cations and anions on the QD surface.⁹² The *L*-PHE incorporated CsPbI₃ QDs also show improved PLQYs, and a longer lifetime, which provide longer diffusion length, high stability, and fewer trap states. This is advantageous in many applications like solar cells and LEDs, *etc.* Liu *et al.*⁶⁵ improved the stability of CsPbI₃ by using the organolead compound trioctylphosphine-PbI₂ (TOP-PbI₂) as a precursor. The room temperature quantum yield was up to 100%. The trapping defect centers, which contribute unwanted nonradiative recombination and result in luminescence quenching, are still a major problem in common quantum dots such as CdSe, and PbS, *etc.* Whereas, the TOP-PbI₃ precursor used for the synthesis of the CsPbI₃ QDs shows negligible electron or hole-trapping effects. This is evidenced by ultrafast kinetic analysis with time-resolved transient absorption spectroscopy.^{65,93} In summary, the stability of the perovskite is improved to some extent by the use of various organic surface capping agents. At the same time, dimensionality also affects the stability of the structures.^{13,87,94} The three black phases of CsPbI₃, α , β , and γ are metastable and likely to transform into the non-perovskite black δ phase. Steele *et al.*⁹⁴ reported that a thin film of the CsPbI₃ black phase is stable as compared to the bulk powder sample. Lower-dimensional perovskites are more stable than bulk 3D perovskite towards humidity.⁹⁵ This reflects that the stability can be improved by reducing the dimension of the structure.

2.4 Optical properties of CsPbX₃

2.4.1 UV-visible absorption and photoluminescence. UV-visible absorption and PL measurement analyses are important

material characterization tools. One can observe the absorption features and gain information about transitions from various energy levels of atoms/molecules, and determine the optical bandgaps of the materials, *etc.*, using absorption and PL measurements. The bandgap of halide perovskites can be tuned in the entire visible spectral region by changing the halide composition. The photographs of CsPbX₃ in hexane solution under room light (top) and UV lamp (bottom) illumination are shown in Fig. 6(a).⁹⁶ The CsPbX₃ (X = Cl, Br, I) showed absorptions in the wavelength region ranging from 390–680 nm.^{57,96} The PL measurement showed that the emission maximum of CsPbCl₃ was ~410 nm, which was further red-shifted after the partial/complete substitution of Cl⁻ ions by Br⁻ to I⁻ ions.^{57–59,96–100} The CsPbI₃ showed the lowest bandgap or highest cut-off absorption wavelength of ~700 nm.^{58,96} The absorption and PL spectra of all-IHPs with different halide compositions are shown in Fig. 6(b). These halide perovskites have narrow emission peaks with FWHM of 11 nm to 37 nm and, therefore, possess the high color purity required for various applications. Table 3 summarizes the emission peak position, FWHM, and PL quantum yields of CsPbX₃ halide perovskite as a function of halide compositions.

Apart from the halide concentration, the size of the NCs also affects the optical properties of all-IHPs.^{57,101,102} With larger NCs, the emission peak and absorption band-edge shift towards longer wavelength. The size of the NCs also depends upon the cationic and anionic radii, larger ions increase the crystal size and *vice versa* for the same synthesis conditions. These effects were also observed in all-IHPs QDs. Fig. 7(a-c) show the variation in absorption and emission peaks of CsPbI₃ as a function of QDs size, and the corresponding morphologies are indicated in Fig. 7(d-f).¹⁰³ Similar variations in absorption and emission spectra were also observed in CsPbBr₃ QDs and are indicated in Fig. 7(g).⁵⁷

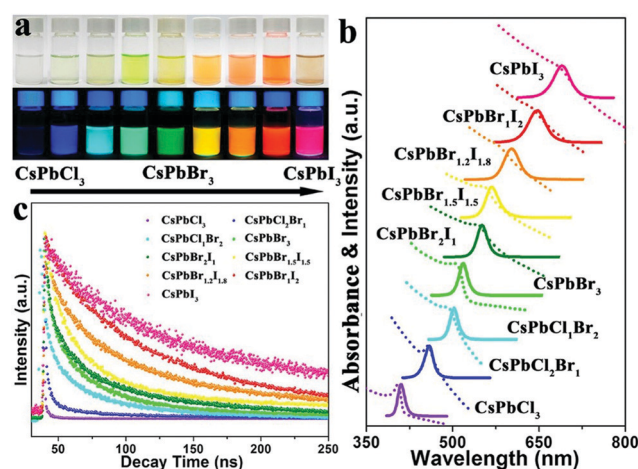


Fig. 6 Colloidal CsPbX₃ (X = Cl, Br, and I) NCs showing a change in the absorption and emission properties as a function of halide concentration. (a) Photographs of CsPbX₃ in hexane solution illuminated under room light (top), and UV lamp (bottom). (b) UV-visible absorption (dotted line), and PL spectra of CsPbX₃, and (c) PL lifetime of CsPbX₃ NCs. Reproduced with permission from ref. 96. Copyright©2017, American Chemical Society.

Table 3 PL properties of CsPbX₃ halide perovskites. Reproduced with permission from ref. 58. Copyright©2018, Nature

Sample	Emission peak (nm)	FWHM (nm)	PLQY (%)
CsPbCl ₃	410	11.7	26.0 ± 0.3
CsPbCl ₂ Br	444	15.5	35.6 ± 0.4
CsPbCl _{1.5} Br _{1.5}	464	16.3	61.8 ± 0.4
CsPbCl ₁ Br ₂	481	17.9	61.4 ± 0.8
CsPbBr ₃	520	20.3	79.8 ± 0.9
CsPbBr ₂ I ₁	587	28.2	71.2 ± 0.5
CsPbBr _{1.5} I _{1.5}	631	29.4	62.7 ± 0.2
CsPbBr ₁ I ₂	660	29.9	58.5 ± 0.7
CsPbI ₃	700	37.0	57.5 ± 0.4

The smaller the particle size, the higher the PLQYs, which is beneficial for light-emitting diodes.^{65,104} Whereas, for the perovskite QDs with size less than the exciton Bohr diameter (D_B), the PLQYs decrease as observed by Kim *et al.*¹⁰⁵ PLQYs for 5 nm perovskite QDs was about 68%, and 62% for 3 nm. For the small perovskite QDs, the surface-to-volume ratio increased, which promoted the creation of surface traps for the exciton. This led to trap-assisted nonradiative recombination at the surface and resulted in a decrease in PLQYs. The variation in the bandgap with quantum dot size can be modeled using effective mass approximation (EMA), where the confinement energy is given by the following:

$$\Delta E = \frac{\hbar^2 \pi^2}{2m^* r^2} \quad (2)$$

where m^* and r are the reduced mass of the exciton and the particle radius, respectively. The value of ΔE accounts for the blue-shift in the emission peak and absorption edge.¹⁰⁴ The bandgap of the CsPbBr₃ as a function of quantum dot size is shown in Fig. 7(h); the square box is the experimental data and the continuous line is the EMA model fitted curve.⁵⁷ A small Stokes shift, which is a measure of the energy difference between the peaks of exciton absorption and emission, was observed in all-IHPs. This indicates that a direct band-edge radiative recombination process is taking place in the resulting structure.

2.4.2 The optical bandgap and photoexcited exciton lifetime. In the CsPbX₃ perovskite, the valence band maximum (VBM) is formed by the antibonding interactions of Pb 6s and X np ($n = 3: \text{Cl}, 4: \text{Br}, 5: \text{I}$) orbitals dominated by X np orbitals.^{106,107} The conduction band minimum (CBM) is formed by the antibonding interaction of the X np and Pb 6p orbitals, with the dominant contribution being from the Pb 6p orbital, whereas the A-site atoms have an almost negligible effect on the VBM and CBM. In CsPbX₃, for X = Cl to Br to I, the VBM shifts toward higher energies as the energy of the X np orbital increases, and at the same time, the CBM shifts towards the region of lower energies.¹⁰⁷ The orbital overlap between two atoms determining the bandgap of the configuration is inversely related to the sum of the ionic radii of the two atoms involved in bandgap formation. The sum of the ionic radii of Pb⁺-Cl⁻ is small as compared to the Pb⁺-Br⁻ and Pb⁺-I⁻,

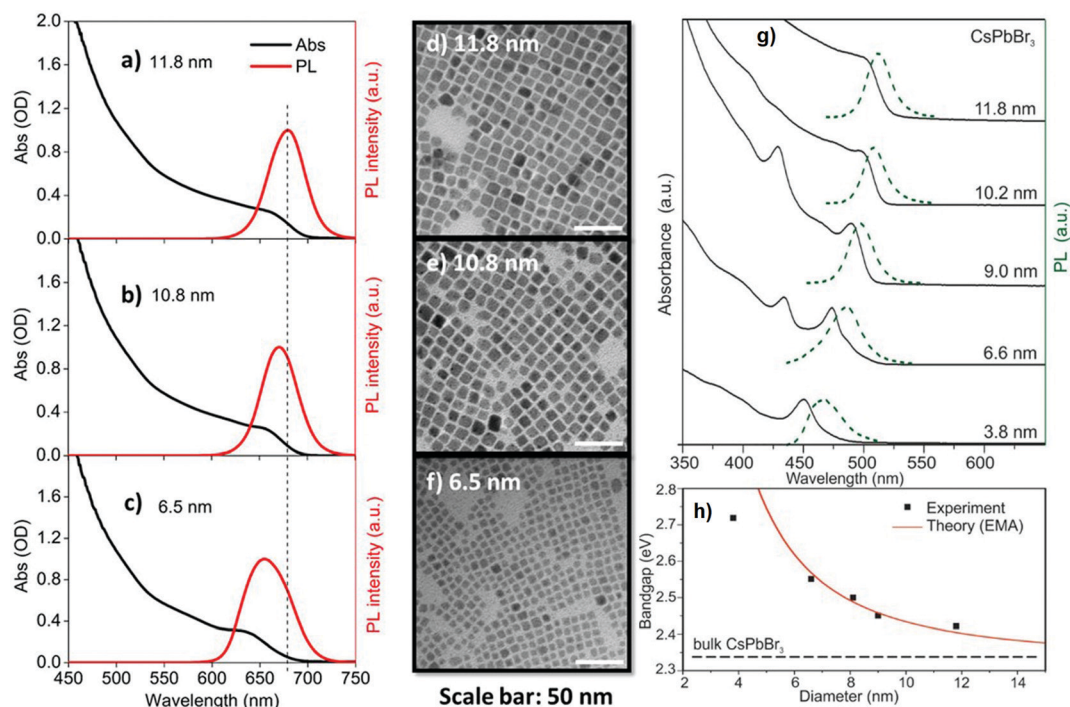


Fig. 7 Optical properties and morphology of CsPbI₃ perovskite QDs. Absorption (black) and emission (red) spectra [(a–c)] of CsPbI₃ perovskite QDs with average sizes of 11.8 ± 1.6 nm, 10.8 ± 1.5 nm, and 6.5 ± 1.1 nm, respectively. (d–f) The corresponding TEM images of three QDs; scale bars in (d–f): 50 nm. Reproduced with permission from ref. 103. Copyright©2019, AIP Publishing. (g) Absorption and emission spectra of CsPbBr₃ plotted in the same image as a function of quantum dot sizes. (h) Variation of the bandgap of CsPbBr₃ as a function of quantum dot sizes, fitted with the EMA model. Reproduced with permission from ref. 57. Copyright©2015, American Chemical Society.

Table 4 Optical bandgap of various inorganic halide perovskites film

Perovskite structure	Optical bandgap (eV)	Synthesis techniques
CsPbCl ₃	3.0	Chemical vapor deposition ¹¹⁰
CsPbBr ₃	2.33–2.34	Vacuum thermal evaporation ⁶²
CsPbBr ₂ I	2.05	Dual source thermal evaporation ¹¹¹
CsPbI _{1.8} Br _{1.2}	1.88	Spin coating ¹¹²
CsPbI ₂ Br	1.9	One-step spray-coating ¹¹³
CsPbI ₂ Br	1.86	Spin coating ¹¹²
CsPbI _{2.2} Br _{0.8}	1.83	Spin coating ¹¹²
CsPbI _{2.4} Br _{0.6}	1.80	Spin coating ¹¹²
CsPbI _{2.7} Br _{0.3}	1.76	Spin coating ¹¹²
CsPbI ₃	1.7	Spin coating ¹¹⁴

resulting in a high degree of orbital overlap and thus a higher bandgap in Pb⁺–Cl[–]. Table 4 summarizes the optical bandgap of some of the all-IHPs. The small variation in bandgap may be observed for the same composition when the synthesis method followed is different. However, if we change the A-site cation (keeping B and X site atom fixed) for comparison, it will affect the bandgap. The band of FAPbI₃ is 1.48 eV, which is less than the bandgap of MAPbI₃ (1.58 eV), whereas the bandgap of CsPbI₃ is 1.7–1.8 eV.¹⁰⁸ The bandgap of the FA-based hybrid perovskite FAPbX₃ is smaller than the MA-based MAPbX₃, and is smaller than CsPbX₃. In the MA-based hybrid perovskite, the bandgap changes from 2.28 eV (MAPbBr₃) to 1.58 eV (MAPbI₃) in MAPbI_xBr_{1–x} on replacing Br with I;¹⁰⁹ however, the bandgap variation trend in MAPbX₃ is the same as CsPbX₃.

The variation in the photoluminescence quantum yields (PLQYs) in CsPbX₃ with halide composition has been studied by many groups. A literature survey indicated the clear trends of PLQYs from low to high with the partial or complete replacement of the Cl composition by Br, whereas, with the partial or complete replacement of Br by I, the PLQYs decreased. Based on the reported data, we predicted that the PLQY for the Cl-based all-inorganic halide perovskite (CsPbCl₃) was low and increased towards the Br-based all-IHPs maximum for CsPbBr₃; this again decreased towards I-based all-IHPs. As can be seen from Table 3, the PLQY value of the CsPbCl₃ is a minimum of about 26%.⁵⁸ It increased after the partial replacement of Cl[–] ions by Br[–] ions and attained the maximum value of about 80% for CsPbBr₃. Further, the substitution of I-ions at Br-sites resulted in a decrease in PLQYs as CsPbI₃ shows PLQYs of about 58%. However, the synthesis method and the type of precursor used for the synthesis of the particular CsPbX₃ perovskite affected the PLQYs as well as the stability.^{115–118} Zhang *et al.*¹¹⁵ used the phenyl-phosphonic dichloride (PhPOCl₂) as a “three precursor” source to synthesize the CsPbCl₃ NCs using the hot injection (usually two precursors are used) method. The PhPOCl₂ precursor-based CsPbCl₃ NCs showed 71% PLQYs with increased stability. Similarly, the use of surface capping agents and the dimensionality of the perovskite structure also affects the PLQYs and stability even for the same CsPbX₃ compositions.^{116,119–122} Dutta *et al.*¹¹⁶ reported the near-unity PLQYs in CsPbX₃ (X = Cl, Br, I) NCs. To achieve near-unity PLQYs, the oleylammonium halide was used as a precursor. The oleylammonium halide acts

as both a halide source and surface capping ligand and thus helps to increase the PLQYs of CsPbX₃ (X = Cl, Br, I) NCs by controlling the reaction temperature. The near-unity PLQYs was also achieved by doping metal ions into the all-IHPs discussed in the lanthanide and other metal ion-doped CsPbX₃ section.^{123,124}

The photoexcited exciton lifetime is the time in which the number of electrons in the particular excited state is reduced to 1/e times the maximum population in that state. The radiative lifetime of the CsPbCl₃ is low and increases towards a high atomic number halide ion with maximum radiative lifetime for CsPbI₃.^{57,96,125,126} The PL lifetime variation trends in all-IHPs with different halide compositions are shown in Fig. 6(c). The PL decay lifetime for CsPbX₃ in the band-edge exciton varies from 1.8–81.1 ns, measured by the pico-second pulsed laser of excitation wavelength 397 nm.⁵⁸ The PL decay lifetimes for CsPbCl_{3–x–y}Br_xI_y are 1.8 ns, 3.5 ns, 8.9 ns, 8.2 ns, 21.1 ns, 41.1 ns, 66.2 ns, 75.0 ns, 81.1 ns for (x, y) = (0.0, 0.0), (1.0, 0.0), (1.5, 0.0), (2.0, 0.0), (3.0, 0.0), (2.0, 1.0), (1.5, 1.5), (1.0, 2.0), and (0.0, 3.0), respectively. It was observed that the all-IHPs with a large bandgap (CsPbCl₃) decays faster as compared to a low bandgap (CsPbI₃).⁵⁷ The radiative lifetime can be increased by reducing the thermal and concentration quenching effect. Thermal quenching is related to the temperature under analysis. Time-resolved PL study of CsPbX₃ QDs, prepared by using the organolead compound precursor trioctylphosphine-PbI₂ (TOP-PbI₂), showed that the photoexcited exciton lifetime was much longer, which is a clear indicator of the reduction of the quenching defects.⁶⁵

2.4.3 Exciton binding energy and anisotropy. The coulombic attraction between electrons and holes is also attributed to exciton binding energy. The optoelectronic properties of semiconductors pretty much depend on their exciton binding energy.¹²⁷ In semiconductor nanostructures, the quantum confinement and the Coulomb interaction between electrons and holes are the two factors that affect the exciton binding energy. The quantum confinement depends on the nanostructure's size and shape. On the other hand, the Coulomb interaction is associated with the static dielectric constant of the material forming the nanostructure. Due to the confinement effect, the electrons and the holes localize, thereby increasing the exciton binding energy and oscillator strengths. The characteristic information about excitons can be obtained by applying external perturbation to the system, such as an electric or magnetic field. An applied magnetic field causes spin splitting of the spectroscopically observed energy levels and is directly proportional to the magnitude of the applied field. At the same time, it also increases the energy of the spin-split levels, called a diamagnetic shift. With an applied magnetic field, the quadratic energy shift in the exciton emission is observed. This gives information about the effects of quantum confinement and the Coulomb interactions in semiconductor nanostructures. In the presence of a magnetic field, the exciton energy is given as follows:¹¹⁰

$$E_{\pm}^n = E_0^n \pm \frac{1}{2} g_{\text{eff}} \mu_B B + \sigma_{\chi}^n B^2 \quad (3)$$

where E_0^n is the n th exciton state unperturbed energy, g_{eff} is the effective exciton Lande factor, μ_B is the Bohr magneton, B is the applied magnetic field, and σ_X^n is the coefficient of the diamagnetic shift. The second term in the above equation represents Zeeman splitting, which increases the degeneracy of the exciton state. The third term represents the diamagnetic shift. The energy positions of the states $n = 1$ and $n = 2$ were fitted using the above equation, which gave $g_{\text{eff}} = 0.8$ and diamagnetic shift coefficient $\sigma_X^1 = 0.64 \pm 0.05 \mu\text{eV T}^{-2}$ and $\sigma_X^2 = 2.0 \pm 0.2 \mu\text{eV T}^{-2}$ for CsPbCl₃. The diamagnetic shift coefficient for CsPbCl₃ (high bandgap perovskite) is lower than CsPbBr₃ and CsPbI₃ (low bandgap perovskites).⁸³ The low value of the diamagnetic shift coefficient for CsPbCl₃ is due to the higher binding energy and lower Bohr radius.¹¹⁰

Another important aspect of CsPbX₃ is their anisotropic behavior that indicates a change in the different properties in different crystallographic directions. Zhao *et al.*¹²⁸ studied the Young's moduli of CsPbI₃ and CsPbBr₃ along different directions, which were found to be the same. On the other hand, CsPbBrI₂ and CsPbBr₂I showed the isotropic nature of Young's moduli along the [001] and [010] directions, and along the [100] and [010] directions, respectively (see Fig. 8). In CsPbBr₂I and CsPbBrI₂, the transport properties (electron and hole mobilities) are superior along [001] in both structures. In this direction, fewer carriers can be captured by the traps during transport. The superior properties of the crystal with [001] orientation may be more suitable for the applications of transistors, light-emitting diodes, photodetectors, solar cells, *etc.* Optical properties such as the extinction coefficient and refractive index of CsPbBr₂I and CsPbBrI₂ also show anisotropic behavior. The extinction coefficients of CsPbBr₂I and CsPbBrI₂ along the [001] direction are greater than that along the [100] direction. Therefore, photon absorption along the [001] direction is greater, resulting in the larger current density and better

spectral responsibility that are required in optoelectronic applications.

The anisotropy-dependent photo-response properties in CsPbBr₃ single-crystal thin-film have been studied by Wang *et al.*⁸⁹ The CsPbBr₃ film showed anisotropic behavior towards absorption and emission spectra, also verified by using first-principles studies. The absorption and emission intensity of CsPbBr₃ film on ZnSe were recorded using circularly polarized light in different polarization directions. The absorption and emission reached their maximum values for the polarization angle 0° while the minimum was observed for 90°. On moving the polarization angle from 0–180°, these again reached a maximum value at 180°. The polarization-dependent photosensitivity of the sample reported was 200 A W⁻¹, showing a fast photo-response time of 20 ms, and the current ratio for the on/off mode was about 10⁴. The anisotropy-dependent absorption, emission and photoresponsivity of the film are indicated in Fig. 9(a), (b) and (c), respectively.

The anisotropy-dependent optical parameter variations were also observed in the nanowires (NWs).¹³⁰ The PL of CsPbBr₃ NWs was studied by applying a polarized excitation field E_0 perpendicular to the long axis of CsPbBr₃ NWs. The PL spectra of 15 nm thick and 250 nm thick NWs excited at 405 nm for polarization angles of 0° and 90° are shown in Fig. 10(a). The polar plots of the polarization-dependent PL intensity of 15 nm thick and 250 nm thick NWs excited at 405 nm are shown in Fig. 10(b) and (c), respectively. Fig. 10(d and e) are the respective optical PL images of two NWs of thickness 15 nm (scale bar 250 nm), and 250 nm at different polarization directions. It was observed that the PL intensity in the parallel polarization is five times higher than the perpendicular polarization for 15 nm thick NWs, which confirmed the anisotropy effect. The thickness-dependence study of NWs showed that higher anisotropy was attained for 15 nm thick NWs as compared to 250 nm thick NWs.

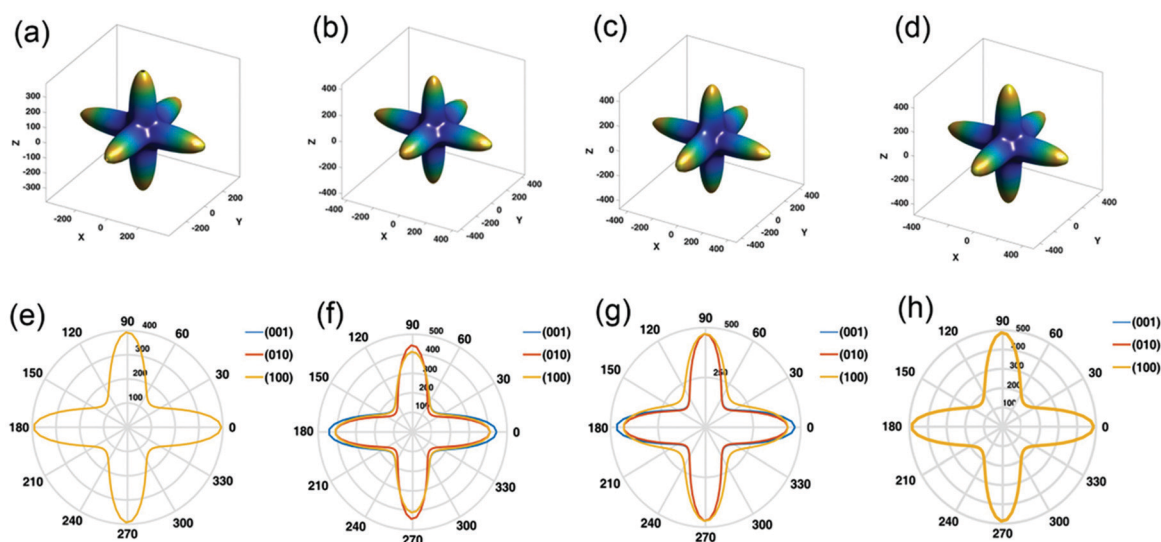


Fig. 8 3D Young's modulus: (a) CsPbI₃, (b) CsPbI₂Br, (c) CsPbIBr₂, and (d) CsPbBr₃. 2D Young's modulus: (e) CsPbI₃, (f) CsPbI₂Br, (g) CsPbIBr₂, and (h) CsPbBr₃. Reproduced with permission from ref. 128. Copyright©2020, Wiley Online Library.

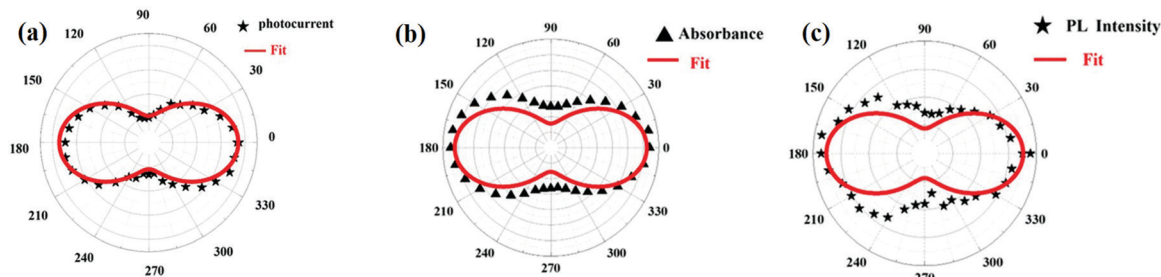


Fig. 9 The polarization dependence polar plot of (a) absorption and (b) PL spectra for CsPbBr₃ film. Black triangles and stars represent the experimental data and solid red lines are fitted curves. (c) The polarization effect on current intensity (bias voltage is 5 V and light intensity is 60 mW cm⁻²). Reproduced with permission from ref. 129. Copyright©2019, Wiley Online Library.

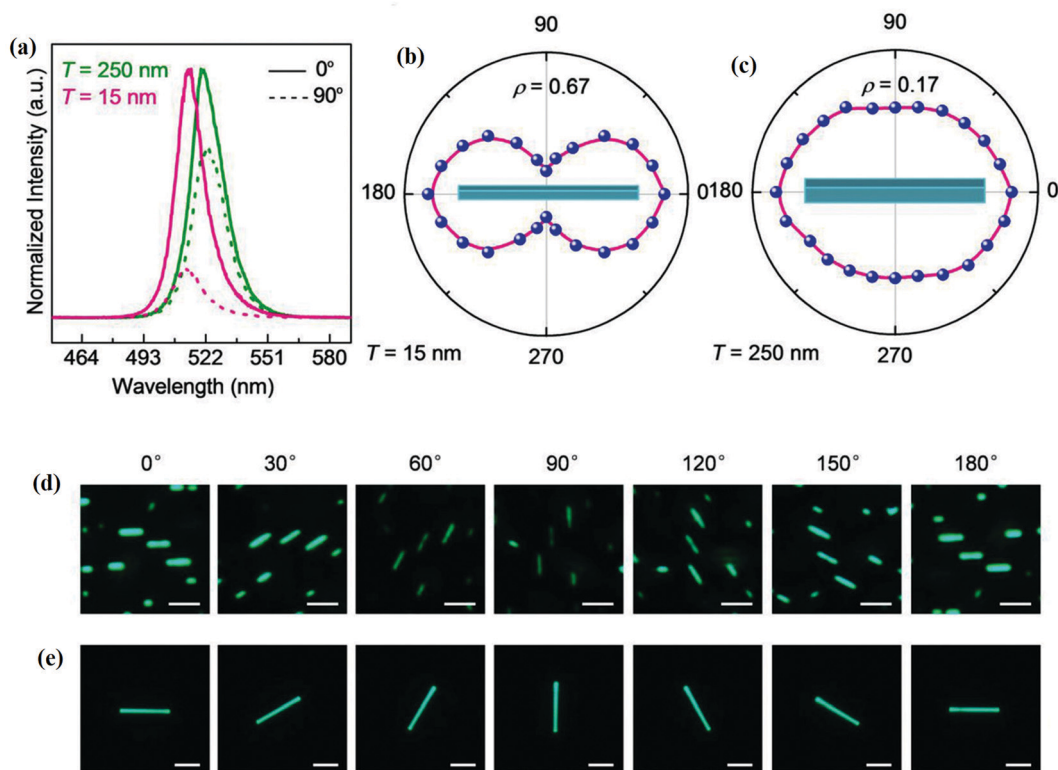


Fig. 10 (a) PL spectra; (b) and (c) polarization dependence PL intensity polar plots (polarization angle 0° represents the polarization field parallel to the NWs) of 15 nm and 250 nm NWs excited at 405 nm. The optical PL images of NWs at different polarization directions of NWs thickness (d) 15 nm (scale bar 250 nm), and (e) 250 nm (scale bar 3 μm). Reproduced with permission from ref. 130. Copyright©2018, Wiley Online Library.

3. Metal ion-doped CsPbX₃

All IHPs have been doped with different types of metal ions such as alkali metals, alkaline earth metals, transition and post-transition metals, and lanthanides. Among these metal cations, lanthanide doping is unique in the sense that they exhibit discrete emission in a wide spectral region ranging from the UV-visible to the near-infrared (NIR) region. These additional optical features bring multifunctionality to IHPs, particularly for emerging applications like NIR and white light-emitting diodes, NIR emitters, NIR cameras, optical temperature sensing, optical data encoding, *etc.* On the contrary, non-lanthanide metal doping only has been used to improve the

existing applications, particularly for LEDs/WLEDs and solar cells. In this review, we have covered metal doping in two different sections, *i.e.*, non-lanthanide metal-ion-doped IHPs (CsPbX₃) and lanthanide-ion-doped IHPs. However, the main focus is to highlight the effect of lanthanide doping in more detail.

3.1 Non-lanthanide metal ion-doped CsPbX₃

Metal ions (M-ion), other than lanthanides, such as alkali metal cations Li⁺,¹³¹ Na⁺,¹³² K⁺,^{133,134} and Rb⁺,¹³⁵ alkaline earth metal cations Mg²⁺,¹³⁶ and Ca²⁺,¹³⁷ transition metals Zn²⁺,^{138,139} Mn²⁺,¹⁴⁰⁻¹⁴³ Ni²⁺,^{144,145} Cu²⁺,^{146,147} Ti³⁺,^{148,149} Y³⁺,¹⁵⁰ and

Cd^{2+} ,¹²⁴ post-transition metal Sn^{2+} ,¹⁵¹ *etc.*, have also been incorporated with the all-IHPs. These metal ions also improve the optoelectronic properties and the stability of IHPs against various environments. The alkali metal cations doped into the all-IHPs take the A-sites, *i.e.*, the Cs^+ position, whereas the alkaline earth metal cations, transition metals, and post transition metals take the B-site *i.e.*, the Pb^{2+} position. B-site doping largely affects the optoelectronic properties as compared to A-site doping.¹⁵² The Mn^{2+} doping in place of Pb^{2+} into the CsPbX_3 reduces the toxicity and increases the PLQYs and stability. As explained, the α - CsPbI_3 perovskite, which shows good optoelectronic behavior, is unstable and is most likely to transform into the non-perovskite phase δ - CsPbI_3 having poor optoelectronic properties. Mn^{2+} doped into CsPbI_3 NCs stabilizes the α - CsPbI_3 phase.¹⁵³ It also improves the stability against UV irradiation as compared to the undoped CsPbI_3 NCs. It exhibits band edge excitonic d-d transitions and results in orange luminescence bands. However, Mn^{2+} -ion incorporation gives new emission bands, which result in impure light emission that limits practical applications. Sn^{2+} also takes the Pb^{2+} site and is less toxic than Pb^{2+} ; however, Sn^{2+} is highly unstable and is oxidized to Sn^{4+} .

3.1.1 The effects of metal (non-lanthanide) doping on the optical properties of CsPbX_3

3.1.1.1 Alkali metal ion-doped CsPbX_3 . The alkali metal ions such as Li^+ ,¹³¹ Na^+ ,¹³² K^+ ,^{133,134} Rb^+ ,¹³⁵ *etc.*, have been doped in CsPbX_3 to improve the PLQYs. The alkali metal ion takes the Cs^+ position instead of Pb^{2+} . The doping concentration of alkali metal ion in CsPbX_3 improves the PLQYs up to a certain concentration limit, after which the PLQYs decreases. The average lifetime also varies in the same fashion as PLQYs with the doping of alkali metal ions in different concentrations. The PLQYs and the average lifetime of 1% $\text{Na}:\text{CsPbCl}_3$ QDs are 56.8% and 26.5 ns, respectively.¹³² Both the PLQYs and the lifetime values gradually increase up to a doping of 4% Na ions and the maximum values are attained at 4% Na doping, *i.e.*, 94.2% and 32.2 ns, respectively. Beyond 4% doping concentration of Na, the PLQYs and average lifetime both decrease and the values dropped to 50.4% and 13.1 ns, respectively for 7% $\text{Na}:\text{CsPbCl}_3$ QDs. Similarly, the optimized doping concentration for Rb^+ ions was 9% in CsPbCl_3 for the maximum PLQYs and average lifetime.

3.1.1.2 Alkaline earth metal ion-doped CsPbX_3 . The alkaline earth metal ions are among the dopants for all-IHPs, which are used to improve the optoelectronic properties of the pristine samples. Alkaline earth metal cations take the Pb^{2+} position instead of Cs^+ , and have a large influence on the optoelectronic properties as compared to alkali metal ions that take the Cs^+ position.¹⁵² Chen *et al.*¹⁵⁴ reported that there was no shift in the diffraction peaks for Mg^{2+} , Ca^{2+} and Sr^{2+} -doped CsPbCl_3 NCs as compared to pristine CsPbCl_3 NCs, which confirmed that there is no structural change after doping. However, a slight shift in the diffraction peaks towards low angles for Ba^{2+} -doped CsPbCl_3 NCs was observed. Since the ionic radius of Ba^{2+} (1.35 Å) is larger than Pb^{2+} (1.19 Å), it is less probable that

Ba^{2+} can take the Pb^{2+} position. However, Chen *et al.*¹⁵⁴ confirmed experimentally and theoretically that Ba^{2+} can enter the core region of the lattice of NCs. Because of the large ionic radius, it produces more stress and lattice distortion and consequently, the diffraction peak shifts to lower angle as observed in the XRD pattern of Ba^{2+} - CsPbCl_3 NCs. The PLQYs of the Ca^{2+} -doped CsPbBr_3 NCs was higher as compared to the undoped sample.^{137,154} The X-ray diffraction (XRD) pattern of pristine CsPbX_3 NCs and doped $\text{Ca}^{2+}:\text{CsPbX}_3$ NCs at different doping concentrations are shown in Fig. 11(a) and (b), respectively for $\text{X} = \text{Br}$, and $\text{X} = \text{Br}_1\text{I}_2$. Fig. 11(c) shows the PL spectra of pristine CsPbBr_3 NCs and doped $\text{Ca}^{2+}:\text{CsPbBr}_3$ NCs, whereas Fig. 11(d) represents PL spectra of both pristine $\text{CsPbBr}_1\text{I}_2$ NCs and doped $\text{Ca}^{2+}:\text{CsPbBr}_1\text{I}_2$ NCs. For the doping concentration of Ca^{2+} -ion up to 40%, the PLQYs of the CsPbBr_3 NCs as well as $\text{CsPbBr}_1\text{I}_2$ NCs increase with the concentration.¹³⁷ For example, the values were 37.9% and 72.3% for Ca^{2+} -ion doping concentrations of 10% and 40%, respectively in CsPbBr_3 NCs, whereas the values were 44.0% and 78.7%, respectively in $\text{CsPbBr}_1\text{I}_2$ NCs. Further, for the doping concentrations of Ca^{2+} -ion above 40%, a decrease in PLQYs was observed in both cases and values were 64.5% and 67.7%, respectively in CsPbBr_3 NCs and $\text{CsPbBr}_1\text{I}_2$ NCs for Ca^{2+} -ion concentration of 50%.

The same variation trend was also observed for the average lifetimes indicated in Fig. 11(e and f). The average lifetimes were 49.45 ns and 108.15 ns for Ca^{2+} -ion doping concentrations of 10% and 40%, respectively, in CsPbBr_3 , whereas it was 80.07 ns and 146.25 ns, respectively in $\text{CsPbBr}_1\text{I}_2$. The doping concentration of Ca^{2+} ions above 40% showed a decrease in the average lifetime in both cases. The average lifetimes were 98.96 ns and 106.99 ns, respectively in CsPbBr_3 and $\text{CsPbBr}_1\text{I}_2$ for Ca^{2+} ion concentration of 50%. Thus, the PLQYs and average lifetimes are higher in $\text{CsPbBr}_1\text{I}_2$ as compared to CsPbBr_3 for the same doping concentration of Ca^{2+} ions. This result indicates that the PLQYs and average lifetime can be increased by the partial or complete substitution of Br or I in place of Cl in CsPbCl_3 NCs. The optimized Ca^{2+} doping concentration for the high PLQYs and average lifetime in the host CsPbCl_3 was 10.5%.¹⁵⁴ For the higher doping concentration, the PLQYs and average lifetime decreased in a similar way as discussed above. Similarly, the optimized doping percentage of Mg^{2+} in CsPbCl_3 was 37.9% at which the maximum PLQY value and average lifetime were observed and were 75.8% and 23.931 ns, respectively. For Mg^{2+} doping concentration higher than 75.8%, both the PLQYs and average lifetime decrease.¹³⁶

3.1.1.3 Transition metal ion-doped CsPbX_3 . Transition metals such as Zn^{2+} ,^{138,139} Mn^{2+} ,^{140–143} Ni^{2+} ,^{144,145} Cu^{2+} ,^{146,147} Cd^{2+} , Ti^{3+} ,^{148,149} Y^{3+} ,¹⁵⁰ Cd^{2+} ,¹²⁴ *etc.*, have been used as dopant elements for all-IHPs. The Mn^{2+} ion has been widely used for improving the PLQYs and stability and to reduce the toxicity of Pb-based all-IHPs. The schematic representation of $\text{Cs}(\text{Pb}/\text{Mn})\text{Cl}_3$ is shown in Fig. 12(a). The XRD patterns of Mn^{2+} - CsPbCl_3 QDs with different doping concentrations are shown in Fig. 12(b). Mn^{2+} doped into the CsPbCl_3 exhibited two emission peaks; a narrow emission peak at around 400 nm

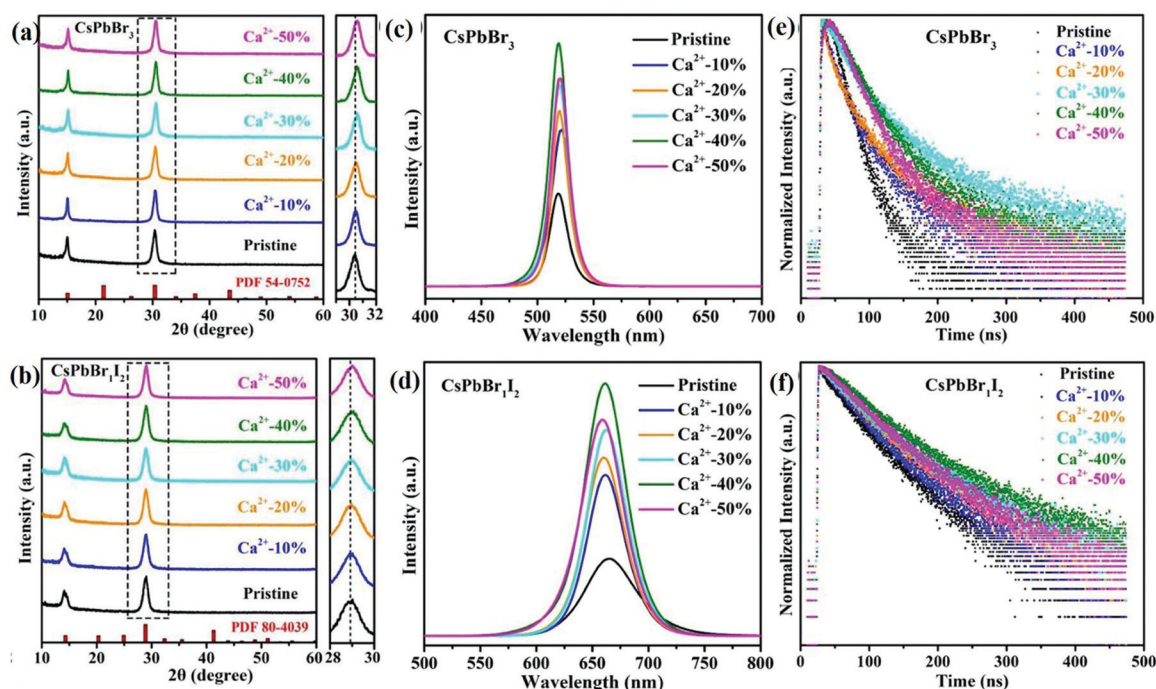


Fig. 11 XRD patterns of (a) pristine CsPbBr₃ NCs and Ca²⁺-CsPbBr₃, (b) pristine CsPbBr_{1.2} NCs and Ca²⁺-CsPbBr_{1.2} NCs with different Ca²⁺ concentrations (enlarged views of the peaks marked by the dotted outline are shown in the right panels). PL spectra of (c) pristine CsPbBr₃ NCs and Ca²⁺-CsPbBr₃, (d) pristine CsPbBr_{1.2} NCs and Ca²⁺-CsPbBr_{1.2} NCs. PL lifetimes of (e) pristine CsPbBr₃ NCs and Ca²⁺-CsPbBr₃, (f) pristine CsPbBr_{1.2} NCs and Ca²⁺-CsPbBr_{1.2} NCs. Reproduced with permission from ref. 137. Copyright©2021, Elsevier.

(due to exciton recombination) and a broad band emission at 600 nm by the Mn²⁺ intrinsic band edge transition as shown in Fig. 12(c).¹⁴⁰ These two peaks appeared at 460 nm and 610 nm for the Mn²⁺-CsPbBr₃ nanoparticles.¹⁵⁵ The orange luminescence was observed at 600 nm in the PL spectra due to the spin-forbidden d-d transition in Mn²⁺.^{140,143} The intensities of the emission peaks at 406 nm and 600 nm can be tailored by the Mn²⁺ doping concentration.^{140,156} For doping up to 20.4% Mn²⁺ (Mn : Pb = 2 : 5) in CsPbCl₃, the intensity corresponding to 406 nm was much higher as compared to the 600 nm emission peak as indicated in Fig. 12(c).¹⁴⁰ For 37.6% Mn²⁺ (Mn : Pb = 1 : 2) doping, both emission peaks showed comparable PL intensities. At higher doping concentrations, the intensity of the emission peak at 406 nm was significantly reduced,

whereas, the intensity of the emission peak at 600 nm increased.^{140,156} The increase in the intensity of the 600 nm emission peak at higher doping concentration was due to the effective energy transfer from CsPbCl₃ to Mn²⁺.¹⁴⁰ However, in the Mn²⁺-doped CsPbI₃ NCs only one emission peak at 679 nm was reported and the peak position varied with the doping concentration.¹⁵³

The PLQYs of the 5.0% Mn²⁺-doped CsPbI₃ increased to 98%. To reduce the toxicity effect of Pb²⁺, a high doping percentage of non-toxic metal is required. Taking toxicity into consideration, Guo *et al.*¹³⁹ reported the optimized doping of (Mn + Zn) into CsPbBr₃. On the basis of “*t*” and “*μ*” values within the structural stability limit, the maximum values of *y* and (*x* + *y*) in CsPb_{1-x-y}Mn_xZn_yBr₃ were 25% and 83%,

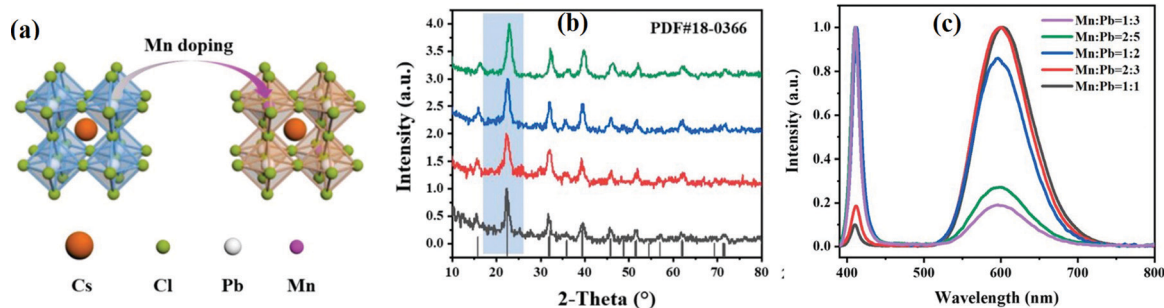


Fig. 12 (a) Schematic representation of Cs(Pb/Mn)Cl₃. (b) XRD pattern of the Mn²⁺-doped CsPbCl₃ QDs for Mn to Pb ratios of 1 : 3 (black), 2 : 5 (red), 1 : 2 (blue), 1 : 1 (green). (c) PL spectra of the Mn²⁺:CsPbCl₃ QDs prepared at different Mn:Pb ratios. Reproduced with permission from ref. 140. Copyright©2021, Elsevier.

respectively. However, (Mn + Zn) co-doping ($x + y$) beyond 50% reduced the visible optical absorption, defect tolerance, and carrier lifetime. Therefore, the maximum doping percentage of (Mn + Zn) in $\text{CsPb}_{1-x-y}\text{Mn}_x\text{Zn}_y\text{Br}_3$ was 50% without reducing the optoelectronic properties of the pristine CsPbCl_3 film. The Mn^{2+} co-doping with Cu^{2+} in CsPbCl_3 was also reported.⁴⁹ The Mn^{2+} - Cu^{2+} co-doped CsPbCl_3 NCs boosted the emission efficiency and 8% PLQYs was achieved.

3.1.1.4 Post transition metal ion-doped CsPbX_3 . Post transition metal Sn^{2+} is also used as a dopant for all-IHPs.¹⁵¹ A major issue with the Sn^{2+} -doped all-IHPs is related to its instability since it is readily oxidized to Sn^{4+} , which limits the practical application of Sn^{2+} -doped all-IHPs. However, researchers have adopted different synthesis approaches with different initial precursors to enhance the stability of Sn^{2+} -doped all-IHPs. The variation trend for the PLQYs and average lifetime with the Sn^{2+} doping concentration in all-IHPs is the same as for other metal doped all-IHPs. As reported by Yan *et al.*,¹⁵¹ initially, the PLQYs and the average lifetime of the Sn^{2+} -doped CsPbBr_3 increased up to the doping concentration of 20% with maximum PLQYs and average lifetime values of 82.77% and 25.26 ns, respectively. For higher Sn^{2+} -doping concentrations, both values decreased. Table 5 summarizes the optoelectronic properties of non-lanthanide metal ion-doped all-IHPs at optimized doping concentrations. However, the listed optoelectronic values of doped CsPbX_3 are predominantly affected by the synthesis methods, precursors used for the synthesis, reaction temperature, reaction time, use of capping ligand, and the doping of different metal ions, *etc.*

3.1.2 Applications of non-lanthanide metal ion-doped CsPbX_3 . Metal ion-doped all-IHPs have been used in various optoelectronic applications. Some widely explored application are for color LEDs,^{136,138,140} and WLEDs,^{137,141,150} *etc.* As usual, metal ion-doped all-IHPs have been explored for photovoltaic applications.⁵²

Researchers have used various metal ion-doped all-IHPs for the fabrication of LEDs using various structural layers. The metal ion-doped LEDs were summarized in detail by

Gao *et al.*¹⁵⁷ It was reported that Zn^{2+} -doped CsPbI_3 with the LED structure $\text{ITO}/\text{ZnO}/\text{PEI}/\text{Zn}:\text{CsPbI}_3/\text{TCTA}/\text{MoO}_3/\text{Au}$ showed a external quantum efficiency of 15.1%.¹⁵⁸ The maximum luminescence described was $40\,000\text{ cd m}^{-2}$ for the Na^+ -doped CsPbBr_3 with $\text{ITO}/\text{PeDOT}:\text{PSS}/\text{perovskite}/\text{TPBi}/\text{LiF}/\text{Al}$ LED structure.¹⁵⁹ Whereas, in the Mn^{2+} -doped CsPbBr_3 , the maximum current efficiency of 6.41 cd A^{-1} was observed with layered structure $\text{ITO}/\text{PeDOT}:\text{PSS}/\text{poly-TPD}/\text{Mn}:\text{CsPbBr}_3/\text{TPBi}/\text{LiF}/\text{Al}$.¹⁶⁰

WLEDs have been constructed mainly by combining non-lanthanide metal ion-doped CsPbX_3 with phosphor materials and LED chips. The CIE coordinates, luminescence efficiency (LE), color rendering index (CRI), and color temperature (CCT) of the non-lanthanide metal ion-doped CsPbX_3 are listed in Table 6.

Recently, Gao *et al.*¹⁵⁷ summarized metal ion-doped all-IHPs solar cells also consisting of different combinations of structural layers. Comparative analysis indicated that Ca^{2+} -doped $\text{CsPbBr}_1\text{I}_2$ had high solar cell parameter values with the solar cell structure $\text{FTO}/\text{TiO}_2/\text{Ca}:\text{CsPbBr}_1\text{I}_2/\text{spiro-OMeTAD}/\text{Au}$. The photo-conversion efficiency (PCE), short circuit current (J_{sc}), open-circuit voltage (V_{oc}) and fill factor (FF) of the $\text{FTO}/\text{TiO}_2/\text{Ca}:\text{CsPbBr}_1\text{I}_2/\text{spiro-OMeTAD}/\text{Au}$ structure were 16.79%, 15.32 mA cm^{-2} , 1.32 V, and 83.29%, respectively.⁵² Other metal ion-doped all-IHPs also showed significant results for solar cell applications, and can be improved by selecting the different structural layers.

3.2 Lanthanide-doped CsPbX_3 : novel properties and emerging applications

3.2.1 Important aspects of lanthanide doping in CsPbX_3 . Lanthanides have been widely explored as optically active dopants in inorganic crystal lattices, which are often insulating in nature.¹⁶³ The doping of trivalent lanthanides (Ln^{3+}) into traditional semiconductor nanocrystals is challenging because of their tetrahedral coordination. Interestingly, CsPbX_3 ($X = \text{Cl}, \text{Br}, \text{and I}$) perovskite nanocrystals provide the octahedral coordination suitable for Ln^{3+} doping. Over the last few years, tremendous success has been achieved in doping Ln^{3+} into CsPbX_3 nanocrystals, combining the excellent optoelectronic

Table 5 The optical and electronic properties of the metal (non-lanthanide)-doped all-inorganic halide perovskite (ABX_3)

Doping ion	M: CsPbX_3	Band gap (eV)	Emission peak (nm) (for λ_{exi} (nm))	Average lifetimes (ns)	Overall PLQYs (%)	Year
Li^+ (NA)	30.0%Li: CsPbBr_3 NCs	—	520	229.80	40.0	2021 ¹³¹
Na^+ (NA)	4.0%Ca: CsPbBr_3 QDs	—	514 (372)	32.20	94.2	2021 ¹³²
K^+ (NA)	4.0%K: CsPbCl_3 QDs	3.05	410 (365)	12.98	10.3	2018 ¹³³
Rb^+ (NA)	9.0%Rb: CsPbCl_3 QDs	3.05	407 (365)	10.20	13.0	2018 ¹³⁵
Mg^{2+} (0.72 Å)	37.9%Mg: CsPbCl_3 NCs	3.084	401	23.931	75.8	2021 ¹³⁶
Ca^{2+} (1.0 Å)	10.5%Ca: CsPbCl_3 NCs	—	407	17.86	77.1	2019 ¹⁵⁴
	40.0%Ca: CsPbBr_3 NCs	—	520.9	108.15	72.3	2021 ¹³⁷
	40.0%Ca: $\text{CsPbBr}_1\text{I}_2$ NCs	—	662.3	146.25	78.0	2021 ¹³⁷
Cu^{2+} (0.73 Å)	2.32%Cu: CsPbCl_3 QDs	—	412 (365)	—	51.0	2021 ¹⁴⁷
Mn^{2+} (0.97 Å)	37.6%Mn: CsPbCl_3 QDs	—	406, 600	10.702	—	2021 ¹⁴⁰
	x%Mn: CsPbBr_3 NPs	—	460, 610 (365)	21.66	64.4	2021 ¹⁵⁵
	x%Mn: $\text{CsPb}(\text{Br}/\text{Cl})_3$ QDs	—	463, 602 (365)	2.66	72.5	2021 ¹⁴¹
Ti^{3+} (0.67 Å)	9.67%Ti: CsPbCl_3 NCs	—	410	22.75	48.4	2021 ¹⁴⁹
Ni^{2+} (0.69 Å)	11.9%Ni: CsPbCl_3 NCs	—	407	18.39	96.5	2018 ¹⁴⁴
Cd^{2+} (0.93 Å)	x%Cd: CsPbCl_3 NCs	—	406 (375)	—	98.0	2018 ¹²⁴
Sn^{2+} (NA)	30.0%Sn: CsPbBr_3 QDs	—	514	25.26	82.77	2021 ¹⁵¹

Table 6 WLED parameters of non-lanthanide metal ion-doped CsPbX₃

WLED structure	CIE coordinate	LE (lm W ⁻¹)	CRI	CCT (K)	Year
Li:CsPbBr ₃ + Eu:BaMgAl ₁₀ O ₁₇ + Eu:CaAlSiN ₃	(0.3318, 0.3383)	—	—	5523	2021 ¹³¹
Y:CsPbBr ₁ I ₂ + Ce:Y ₃ Al ₅ O ₁₂ + InGaN LED chip	(0.34, 0.35)	61	83	—	2022 ¹⁵⁰
Ca:CsPbBr ₁ I ₂ + Ca:CsPbBr ₃ + InGaN LED chip	(0.3366, 0.3376)	92.4	92.2	—	2022 ¹³⁷
Mn:CsPb(Br/Cl) ₃ + InGaN LED chip	(0.39, 0.38)	—	—	—	2021 ¹⁴¹
Ni:CsPbBr _{1-3-x} + Ce:YAG InGaN LED chip	(0.3621, 0.3458)	113.20	94.9	4336	2021 ¹⁶¹
Zn:CsPbBr ₃ + Mn:K ₂ SiF ₆ + blue LED chip	(0.327, 0.336)	36.0	—	5760	2021 ¹⁶²
Sn:CsPbBr ₃ :AgInZnS:InGaN LED chip	(0.41, 0.48)	43.2	89	—	2021 ¹⁵¹

properties of the host with the f–f electronic transitions of the dopants. Charge neutrality, FRET pair formation, multi-functionality and emerging applications are the three major aspects that justify lanthanide doping in all-IHPs.

Charge neutrality consideration: at first the basic conditions that should be fulfilled while doping with another ion are charge neutrality and the size of the dopant. The charge neutrality condition is that the cationic and anionic charges should be the same for the charge balance. However, in some cases, the presence of excess charge is also beneficial for particular applications like solar cells for the charge transport layer. Concerning charge neutrality, lanthanides are remarkable candidates for substitution into the ABX₃ perovskite structure because of their comparable ionic radii with the Pb²⁺ ion (1.19 Å). Hence, in the doping process, the lanthanide replaces the Pb²⁺ ion because of its comparable ionic radius.¹⁶⁴ This could be confirmed experimentally by high-resolution XPS spectra. For example, the high-resolution XPS spectra indicated a decrease in the binding energy of Pb²⁺ 4f_{5/2}, and Pb²⁺ 4f_{7/2} when Eu³⁺ ions were doped.¹⁶⁵ There was very little variation in the binding energies of Cs³⁺ 3d_{3/2}, and Cs³⁺ 3d_{5/2}. In Cl⁻ 2p_{1/2} and Cl⁻ 2p_{3/2}, variation in binding energy was also very small. This indicates that Eu³⁺ ions occupy the Pb²⁺ lattice sites in the host lattice of CsPbCl₃ instead of Cs⁺ and Cl⁻ sites.

Realization of FRET pairs: lanthanide-doped nanoparticles and IHPs QDs can make a FRET (fluorescence resonance energy transfer) pair. In this process, the lanthanide-doped NPs convert low-energy photons (e.g., IR-photons) into photons of high energy through the UC process.^{166,167} These high energy photons are re-absorbed by the perovskite QDs through FRET and thereby, the electron and hole pairs are generated in the perovskite QDs. Finally, the emission of photons takes place from perovskite QDs through exciton recombination. Thus, the emission from perovskite QDs in principle can be achieved

through IR excitation, which opens up a new area of applications.^{58,167}

The FRET process in lanthanide-doped nanoparticles to perovskite QDs requires effective distance control between them, which is a difficult task. Further, the quenching of the upconversion (UC) luminescence intensity by QDs also depends on the absorbance coefficient of the perovskite QDs. Thus, the energy transfer efficiency (η_{ETE}) depends on both the position of the energy level and the effective distance between the emitter and the absorber.⁵⁸

$$\eta_{ETE} = \frac{n_{abs}^X}{n_{em}^{Tm}} = \frac{I_0^{Tm} - I_X^{Tm}}{I_0^{Tm}} \quad (4)$$

I_0^{Tm} and I_X^{Tm} are the integrated intensities of the UCL of Tm³⁺ from the NPs in the absence and presence of CsPbX₃ perovskite QDs, respectively. The integrated intensity is measured with frequencies above the band edge of CsPbX₃. Zheng *et al.*⁵⁸ found that the energy transfer efficiency from LiYbF₄:0.5%Tm³⁺@LiYF₄ core/shell NPs to perovskite QDs increased from 65.5 to 96.6 and 99.9% when the composition of the halide changed from Cl⁻ to Br⁻ and I⁻ ions, and are listed in Table 7. The energy transfer efficiency from the NPs to CsPbCl₃ is low. This may be due to the smaller UV absorbance in CsPbCl₃ as compared to the other CsPbX₃ perovskite QDs, as manifested by their absorption spectra. The UC quantum yields (UCQYs) under 980 nm CW diode laser excitation at a power density of 100 W cm⁻² for pure LiYbF₄:0.5%Tm³⁺@LiYF₄ core/shell NPs and NPs-sensitized CsPbX₃ perovskite QDs with varying halide compositions were studied. The overall UCQYs reported are (0.44 ± 0.07), (0.45 ± 0.10), and (0.36 ± 0.09)% for the chloride, bromide and iodide compositions in the perovskite QDs, respectively. This is indirectly proportional to the PLQYs of the PeQDs.

Multifunctionality and emerging applications: the halide perovskites were initially synthesized for perovskite-based solar

Table 7 Optical and electronic parameters of undoped and lanthanide ion-doped CsPbCl₃. Reproduced with permission from ref. 165. Copyright©2017, American Chemical Society

Doping ion	N/A	Ce ³⁺	Sm ³⁺	Eu ³⁺	Tb ³⁺	Dy ³⁺	Er ³⁺	Yb ³⁺
Ionic radius of dopant (Å)	N/A	1.034	0.964	0.950	0.923	0.881	0.908	0.858
Lattice constant (Å)	3.96	3.94	3.93	3.92	3.90	3.89	3.88	3.87
Absorption peak (nm)	400	395	390	392	390	382	381	375
Band gap (eV)	2.87	2.91	2.94	2.98	3.03	3.05	3.08	3.10
Excitation peak (nm) (for λ_{em} (nm))	368 (410)	385 (430)	470 (603)	360 (620)	400 (555)	372 (575)	400 (548)	390 (982)
Average lifetimes ^a (ns)	4.1	3.7	6.2	6.7	7.1	7.6	8.2	9.1
Overall PLQYs (%)	3.8	24.3	14.1	27.2	31.2	27.6	15.1	142.7

^a Emission decay was monitored at 410 nm.

cells because of their exceptional optoelectronic properties leading to the high efficiency of solar cells.¹⁶⁸ The presence of volatile organic cations in the structure, however, reduces its stability. Therefore, efforts have been made to increase their stability and also to explore these optoelectronic properties for some other novel applications. One of the approaches for making them multifunctional involves the incorporation of lanthanide ions into the perovskite structure.^{169,170} This not only makes halide perovskite suitable for extended applications, but also increases their stability and improves the efficiency of solar cells.^{123,171,172} Huang *et al.*¹⁷³ fabricated NIR light-emitting diodes by Yb³⁺-doped CsPbCl₃ perovskite nanocrystals with excellent long-term stability. Zhang *et al.*¹⁷⁴ reported Yb³⁺-doped CsPbCl₃ nanocrystals that emit strong NIR light at 986 nm and the Yb³⁺/Er³⁺ co-doped CsPbCl₃ nanocrystal has emission at 1533 nm. The PL quantum yield also increased from 5% to 127.8% on doping 2% Yb³⁺-into CsPbCl₃. This shows a high NIR output irradiance of 112 mW cm⁻²@400 mA, which may have great potential in the future as a light source in night-vision cameras. The Eu³⁺ ion doped CsPbI₂Br solar cell was reported by Chen *et al.*⁹⁹ Solar cell efficiency of 12% was achieved with good thermal stability. It was also reported that the Eu³⁺ ion doping into CsPbI₂Br stabilized the γ -CsPbI₂Br phase, which also increased the device performance. The CsPbBr₃ perovskite showed up-conversion phenomena by using BaYF₅ as a sensitizer.¹⁶⁷ The nano-composite of CsPbI₃ and CaF₂:Yb³⁺/Ho³⁺ showed both up-conversion and down-conversion behavior.¹⁶⁶ This can be used in dual-mode bio-imaging applications.¹⁷⁵ The newly emerging applications of lanthanide-doped all-IHPs are in improved solar cell applications (Section 3.2.4.1), the generation of WLEDs (Section 3.2.4.2), NIR-light emitters, NIR LEDs, and NIR cameras (Section 3.2.4.3), optical temperature sensing (Section 3.2.4.4), and as optical encoding material (Section 3.2.4.5).

3.2.2 The effects of lanthanide doping on the stability and structure of CsPbX₃. Lanthanide ion doping into halide perovskites not only brings multiple functionalities but also improves their environmental, thermal- and photo-stability, which have been major concerns for various optoelectronic device applications of all-IHPs. Various mechanisms explain the increase in the stability of the halide perovskites in the presence of lanthanide ions:¹⁷⁶ (i) lanthanide doping can affect the growth kinetics during the synthesis process and result in the formation of a stable perovskite phase.¹⁷⁷ (ii) In metal halide perovskites, (Pb)⁰ and (I)⁰ defects form, which work as recombination centers and also affect the life of the device. Wang *et al.*¹⁷⁸ demonstrated that the incorporation of the europium ion pair Eu³⁺-Eu²⁺ can shuttle electrons and thereby recover the lead and iodide ions (Pb²⁺ and I⁻). This simultaneously increases the efficiency and stability of the device. (iii) Apart from the lanthanide ion doping in halide perovskites, one can use lanthanide complexes, which are easily functionalized over halide perovskites surfaces, to improve the stability and multifunctionality. Chen *et al.*¹⁷² have incorporated europium acetylacetonate [Eu(Ac)₃] into the perovskite precursor CsPbI₂Br and found that Eu³⁺ ions strongly interact with halide plumbates. Some

amount of Eu³⁺ ions were also inserted into the interstices of the CsPbI₂Br lattice, causing an increase in their crystal size and the remaining Eu³⁺ ions accumulated in the grain boundaries. This reduced the phase transformation of γ -CsPbI₂Br to the non-perovskite phase and also increased its performance. (iv) Another mechanism could be the use of a layer of lanthanide complex before the halide perovskite, which can absorb the UV radiation and emit the characteristic emission of the lanthanide ions. In this way it can increase the device stability by masking the halide perovskite from UV light, and also the luminescence at a higher wavelength can be effectively used by halide perovskite. Duan *et al.*¹⁷¹ monitored the photoconversion efficiency (PCE) of undoped and 3% Sm³⁺-doped CsPbBr₃ for 60 days. It was found that under 0% relative humidity at 80 °C, the Sm³⁺-doped CsPbBr₃ retained more than 90% of the initial PCE, whereas, for the undoped CsPbBr₃, the PCE retained only ~80% of the initial value. This revealed the improved thermal stability of the halide perovskite after lanthanide (Sm³⁺) ion doping.

The I⁻-based halide perovskite showed phase transformation from the perovskite structure α to β then to γ and finally to the non-perovskite structure δ phase. Jena *et al.*¹⁷⁹ showed that the incorporation of Eu³⁺ ions stabilized the black α -CsPbI₃ phase with improved photovoltaic performance. Zhang *et al.*¹⁷⁴ reported that the CsPbCl₃:Yb³⁺ NCs solution showed longer photostability than undoped CsPbCl₃ NCs. To demonstrate this, both samples were placed under the continuous irradiation of a 6 W UV (365 nm) lamp and the PL was recorded as a function of time. The undoped CsPbCl₃ NCs showed 80% decrease in PL intensity in 27 h, whereas, the same amount of decay in intensity was observed in 85 h for Yb³⁺-doped CsPbCl₃ NCs. The lanthanide ions occupied the Pb²⁺ ion sites and also reduced the Cs⁺ ion vacancies.¹⁸⁰ This in turn reduced the defect and trap states. Since the stability of halide perovskites and improving the efficiency of optoelectronic devices are still among the focus areas of research, further investigations on the integration of lanthanide ions with halide perovskites are expected to bring exciting outcomes.

3.2.3 The effects of lanthanide doping on the optical properties of CsPbX₃

3.2.3.1 The effects on UV-visible absorption and photoluminescence. The variation in the optical bandgap affects the band-to-band PL of semiconducting materials. The substitution of smaller ions (all lanthanides after Gd³⁺) for the Pb²⁺ ion leads to lattice shrinkage. This causes an increased ligand field within the [PbBr₆]⁴⁻ octahedra, leading to an increase in the bandgap. This effect can be monitored by recording the UV-visible absorption spectrum, which shows a shift in the absorption peak towards higher energy, *i.e.* a blue shift.¹⁸¹ Lanthanide ion doping also increases the stability of the perovskite structure. The effects of lanthanide ion doping on the structural and optical properties in CsPbCl₃ were determined by Pan *et al.*¹⁶⁵ The XRD patterns of the pristine CsPbCl₃ NCs and Ln³⁺-doped CsPbCl₃ NCs are shown in Fig. 13(a). These revealed that lanthanide ion doping preserves the structure of the host but the average crystallite size changes.¹⁶⁵ The average crystallite size decreases linearly towards the higher atomic number of lanthanide ions.¹⁷¹ This also induces a blue

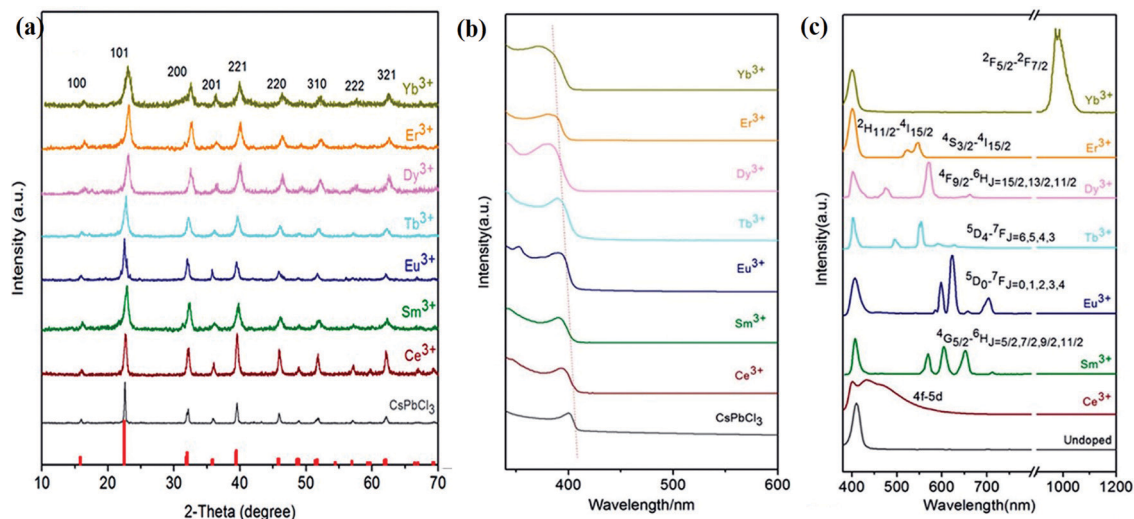


Fig. 13 (a) XRD patterns, (b) absorption spectrum, (c) emission spectra of pristine CsPbCl₃ NCs and lanthanide-doped CsPbCl₃ NCs. Reproduced with permission from ref. 165. Copyright©2017, American Chemical Society.

shift in the PL spectra, *i.e.*, an increase in the binding energy of the structure due to quantum confinements.^{165,171,182} Fig. 13(b) shows that doping smaller-sized lanthanide ions into CsPbCl₃ resulted in the blue shift of the absorption edge.¹⁶⁵ This blue shift was also observed in the emission spectrum, indicating the increased bandgap of Ln³⁺-doped CsPbCl₃ NCs. Table 7 summarizes the optoelectronic properties of the lanthanide-doped CsPbCl₃ NCs.

3.2.3.2 The effects on PL quantum yields and lifetimes. Lanthanide ion doping increases the PLQYs of CsPbCl₃.¹⁶⁵ In the lanthanide-doped CsPbCl₃ structure, defect modification takes place and results in increased PLQYs. It should be noted that the PLQYs of the Yb³⁺-doped CsPbCl₃ crystal was much higher as compared to the other lanthanide dopants.^{165,169} Zhou *et al.*¹²³ considered the different host compositions for lanthanide ion doping. Table 8 shows various combinations of host and lanthanide with their quantum yields, which might be useful in selecting a particular combination of the host and lanthanide. Among the different host and dopant combinations, high PLQY was observed for the Yb³⁺-Pr³⁺-Ce³⁺-doped CsPbCl_{3-x-y}Br_xI_y, and a relatively low PLQY for Yb³⁺-Dy³⁺-doped CsPbCl_{3-x-y}Br_xI_y. The maximum and minimum PLQY were observed for Yb³⁺-Pr³⁺-Ce³⁺-doped CsPbClBr₂ and Yb³⁺-Dy³⁺-doped CsPbI₃.

Time-resolved spectroscopy revealed that the lanthanide-doped CsPbCl₃ has a longer average lifetime than 1.8 ns for

undoped CsPbCl₃.¹⁶⁵ For Yb-doped CsPbCl₃ NCs the average lifetime is 22 ns, which is larger than undoped CsPbCl₃ NCs.¹⁸³ Pan *et al.*¹⁸² reported that the average lifetime for 2.7%Ce:CsPbCl₃ was 5.3 ns. For 0.1% Dy-doped CsPbBr₃, the average lifetime was 27.88 ns, whereas for CsPbBr₃ it was 21.22 ns.¹⁸⁴ The average lifetime increased with Dy concentration and attained a maximum value 54.34 ns for 0.7% Dy-doped CsPbBr₃ and then decreased with further increase in the Dy concentrations to 42.26 ns for 0.9% Dy:CsPbBr₃. An initial increase in average lifetime indicates that the electronic defect-mediated non-radiative transition was effectively reduced due to Dy concentration. The decreased average lifetime at higher concentrations, *i.e.* at 0.9% Dy, was due to the concentration quenching effect of lanthanides. The average lifetime further increased with the higher atomic number of lanthanide ions for a particular CsPbX₃ host. Longer average lifetimes, as well as increased PLQYs, are the consequence of the partial elimination of non-radiative channels in the lanthanide-doped CsPbCl₃.

3.2.3.3 The effect of lanthanide doping concentration on the PL peak intensity of CsPbX₃. The PL peak intensity is a measure of the number of emitted photons. The intensity of PL spectra depends on various parameters such as the type of material, the local surrounding temperature and doping concentration, *etc.* Doping concentration-dependent PL studies of Eu³⁺-doped

Table 8 The PLQYs (in %) of various lanthanide ion combinations in halide perovskite hosts. Reproduced with permission from ref. 123. Copyright©2019, American Chemical Society

	CsPbCl ₃	CsPbCl _{1.5} Br _{1.5}	CsPbClBr ₂	CsPbBr ₃	CsPbBr ₂ I	CsPbBrI ₃	CsPbI ₃
Yb ³⁺	85	117	137	95	75	73	59
Yb ³⁺ -Tb ³⁺	63	102	114	89	64	59	51
Yb ³⁺ -Dy ³⁺	47	78	97	94	58	52	43
Yb ³⁺ -Nd ³⁺	80	115	132	93	71	67	56
Yb ³⁺ -Ce ³⁺	100	146	154	95	72	67	55
Yb ³⁺ -Pr ³⁺	110	148	163	97	73	65	63
Yb ³⁺ -Pr ³⁺ -Ce ³⁺	118	153	173	95	79	72	65

CsPbCl₃ have been carried out by Pan *et al.*⁹² The absorption edge and emission peak showed blue shifts with an increase in Eu³⁺ concentration as shown in Fig. 14. This blue shift is due to the lattice contraction with doping ion concentration.^{165,169,185} Zhou *et al.*¹⁶⁹ confirmed that there was an increase in the bandgap with increasing the doping concentration. The intrinsic transition intensity corresponding to the Eu³⁺ ion increased with the doping concentration. This behavior is because the high doping concentration facilitates efficient energy transfer from the host CsPbCl₃ to Eu³⁺ ions. The PLQYs of the doped CsPbCl₃ initially increased and then decreased with the concentration of Eu³⁺ ions.¹⁶⁵ The maximum PL of Eu³⁺ appeared for the doping concentration of 7.8 mole% (see Fig. 14). The effect of a blue shift in the absorption and emission spectra was observed with the Lu³⁺-doping concentration in Lu³⁺-doped CsPbBr₃ NCs and in Yb³⁺-doped CsPbI₃.^{177,185} Hence, this trend may also be predicted for Ln³⁺-doped CsPbX₃.

The optimized lanthanide doping concentration varies based on the CsPbX₃ host. Also, in the lanthanide-doped CsPbX₃, the PLQY and average lifetime initially increased with Ln³⁺-doping concentration and attained a maximum value. The PLQYs and the average lifetime subsequently decreased for higher doping concentrations. The variation trend for optoelectronic properties like PLQYs, average lifetime, *etc.*, was the same as observed in the case of non-lanthanide metal ions-doped CsPbX₃.

3.2.4 Emerging applications of lanthanide-doped all-inorganic halide perovskites. The halide perovskites have continued to gain importance for photovoltaic and other optoelectronic devices since their inception. Initially, they were investigated for only photovoltaics but now all-IHPs are considered one of the best multifunctional materials. Over the last few years, researchers from the area of photovoltaics have been investigating lanthanide-doped all-IHPs because of their potential to increase the efficiency and the stability of the devices. In spite of photovoltaics and colored (visible and white) light-

emitting diode applications, the lanthanide-doped all-IHPs are being used in many new and emerging fields, which was not possible with undoped all-IHPs, particularly in the field of NIR emission, NIR LEDs, NIR cameras, optical encoding, luminescence-based sensing and non-linear emission processes, *etc.* In this section, we cover some specific applications that are due to the merit of lanthanide doping in CsPbX₃ halide perovskites.

3.2.4.1 Advancements in solar cell application. To analyze the effects of lanthanide ion doping, Duan *et al.*¹⁷¹ used lanthanide ions (Sm³⁺, Tb³⁺, Ho³⁺, Er³⁺, and Yb³⁺) in CsPbBr₃ in the fabrication of solar cells and calculated different solar cell parameters. Table 9 summarizes the solar cell parameters for different devices that use lanthanide-doped all-IHPs. The data indicate that lanthanide doping significantly improves cell performance. They found an ultrahigh open-circuit voltage of ~1.594 V under the one sun illumination for lanthanide ion-doped all-IHPs. The lanthanide doping also improved thermal stability. On exposure to 80% relative humidity in an air atmosphere, the efficiency of the solar cell remained almost unchanged over 110 days. The Ln-doped ABX₃ has been used as one of the layers of the solar cell structure, FTO/c-TiO₂/m-TiO₂/Ln:CsPbX₃/carbon. The results from Table 9 indicate the potential of lanthanide-doped all-IHPs materials for solar cell applications.

3.2.4.2 Lanthanide-doped all-inorganic halide perovskites for WLEDs. The halide perovskite QDs show a very high PL quantum yield, which allows various novel optoelectronic applications. One of their fascinating applications is in the fabrication of tunable colored LEDs. In recent years, lanthanide-doped all-IHPs have also been actively explored for this purpose. For example, Nd³⁺ doping into CsPbBr₃ NCs shifts the emission peak from 515 nm to 459 nm.¹⁸⁹ After the encapsulation of green light-emitting CsPbBr₃ NCs and blue-light emitting CsPbBr₃:xNd³⁺ (x = 7.2%) NCs in the PMMA host and after

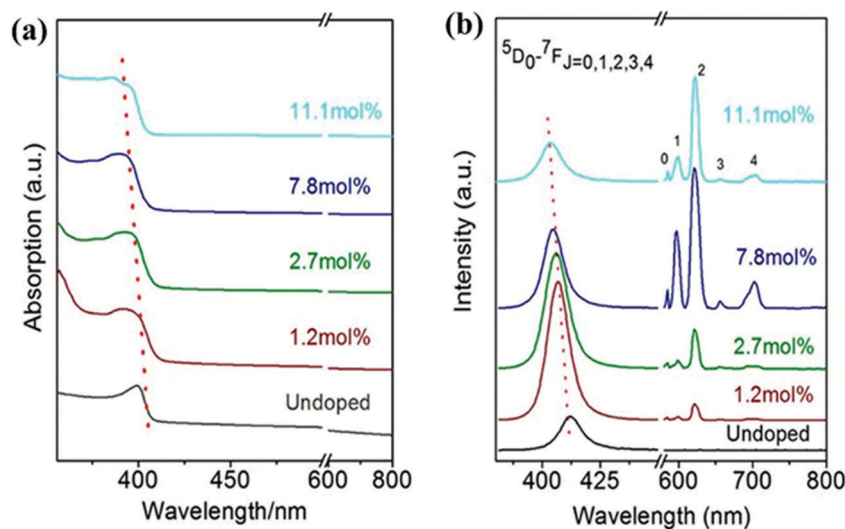


Fig. 14 (a) Absorption and (b) emission spectra under 365 nm excitation of CsPbCl₃ and different doping concentrations of Eu³⁺ in the CsPbCl₃ structure under 365 nm excitation. Reproduced with permission from ref. 165. Copyright©2017, American Chemical Society.

Table 9 Photovoltaic parameters of lanthanide-doped inorganic halide perovskites (characterization was done using solar simulator AM 1.5G with 100 mW cm⁻² light intensity)

Halide perovskite	Dopant	Cell structure	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	Year
CsPbBr ₃	Eu ²⁺	FTO/c-TiO ₂ /m-TiO ₂ /CsPb _{1-x} Eu _x Br ₃ /carbon	6.33	1.4523	79.19	7.28	2021 ¹⁸⁶
CsPbBr ₃	Yb ³⁺	FTO/c-TiO ₂ /m-TiO ₂ /CsPb _{0.97} Yb _{0.03} Br ₃ /carbon	7.45	1.536	80.20	9.20	2018 ¹⁷¹
CsPbBr ₃	Er ³⁺	FTO/c-TiO ₂ /m-TiO ₂ /CsPb _{0.97} Er _{0.03} Br ₃ /carbon	7.46	1.563	82.80	9.66	2018 ¹⁷¹
CsPbBr ₃	Ho ³⁺	FTO/c-TiO ₂ /m-TiO ₂ /CsPb _{0.97} Ho _{0.03} Br ₃ /carbon	7.45	1.572	83.20	9.75	2018 ¹⁷¹
CsPbBr ₃	Tb ³⁺	FTO/c-TiO ₂ /m-TiO ₂ /CsPb _{0.97} Tb _{0.03} Br ₃ /carbon	7.47	1.588	84.80	10.06	2018 ¹⁷¹
CsPbBr ₃	Sm ³⁺	FTO/c-TiO ₂ /m-TiO ₂ /CsPb _{0.97} Sm _{0.03} Br ₃ /carbon	7.48	1.594	85.10	10.14	2018 ¹⁷¹
CsPbI ₂ Br	Eu ³⁺	ITO/NiO/CsPb _{0.995} Eu _{0.005} I ₂ Br/PC ₆₁ BM/Ag	15.30	1.130	70.50	12.10	2021 ¹⁷²
CsPbI ₂ Br	Eu ³⁺	FTO/c-TiO ₂ /m-TiO ₂ /CsPb _{0.95} Eu _{0.05} I ₂ Br/spiro-OMeTAD/Au	14.63	1.223	76.60	13.71	2019 ¹⁸⁷
CsPbI ₃	Eu ³⁺	FTO/TiO ₂ /CsPb _{0.95} Eu _{0.05} I ₃ /spiro-OMeTAD/Au	11.10	0.890	68.00	6.80	2018 ¹⁷⁹
CsPbI ₃	Yb ³⁺	FTO/TiO ₂ /CsPb _{0.95} Yb _{0.05} I ₃ /PTB7/MoO ₃ /Ag	13.25	1.250	75.00	12.42	2019 ¹⁸⁰
CsPbI ₃	Yb ³⁺	FTO/TiO ₂ /CsPbI ₃ :5%YbCl ₃ /spiro-OMeTAD/Ag	18.40	1.130	60.00	12.40	2020 ¹⁸⁸

their deposition on a UV-LED having a red-emitting CsPbBr_{1.2}I_{1.8}/PMMA, WLEDs can be realized. The fabricated WLEDs have excellent color coordinates (0.34, 0.33) and NTSC value of 122% with a cool-white correlated color temperature of 5310 K. Yuan *et al.*¹⁸⁵ fabricated WLEDs by integrating Yb³⁺-doped CsPbI₃ with the GaN LED blue-chip having the Y₃Al₅O₁₂:Ce³⁺ phosphor. The PL spectrum of Yb³⁺-doped CsPbI₃ coated over GaN is shown in Fig. 15(a). The schematic of the WLEDs and color coordinates for WLEDs are shown in Fig. 15(b and c), respectively.

Pan *et al.*¹⁸² compared the performance of WLEDs prepared using various lanthanide ion pairs in halide perovskites. They considered CsPbCl₃:2.7% Ce³⁺:7.8% Eu³⁺, CsPbCl_{1.8}Br_{1.2}:2.7% Ce³⁺:7.8% Eu³⁺, CsPbCl₃:2.7% Ce³⁺:7.8% Sm³⁺ and CsPbCl_{1.8}Br_{1.2}:2.7% Ce³⁺:7.8% Sm³⁺ for their studies. Among these four pairs, the maximum luminous efficiency (LE) and color rendering index (CRI) were 36 lm W⁻¹ and 92, respectively for CsPbCl_{1.8}Br_{1.2}:2.7% Ce³⁺:7.8% Eu³⁺. Zhu *et al.*¹⁸⁴ reported Dy³⁺-doped CsPbBr₃ quantum dots to demonstrate WLEDs. For the generation of WLEDs, the green-emitting Dy³⁺-doped CsPbBr₃ was incorporated with the red-emitting Mn²⁺-doped K₂SiF₆ phosphor and blue-emitting InGaN chips. The CIE coordinates of the fabricated WLEDs reported were (0.2881, 0.3001) and the NTSC value was 126.3% on application of a 40 mA drive current. The Ce³⁺ ion incorporation into the CsPbCl₃ NCs enhanced the blue and green components.¹⁸² It also behaved as a sensitizer for ions such as Eu³⁺ and Sm³⁺ and promoted red emission. This opens up future applications for WLED based on phosphor converted all-IHPs. Table 10

summarizes the lanthanide ion-doped CsPbX₃-based WLED parameters for the optimized lanthanide doping concentration.

3.2.4.3 Lanthanide-doped halide perovskites for NIR emission and NIR LEDs. All-IHPs are known for their characteristic emission in the visible region. Lanthanide doping adds some UV and infrared components of the electromagnetic spectrum due to 4f–4f transitions of different lanthanide ions. For example, the Yb³⁺-doped CsPbBr₃ NCs showed NIR emission;¹⁹⁰ the NCs were encapsulated with SiO₂. The strong NIR (985) emission occurred from Yb³⁺ ions. This is the intrinsic luminescence of Yb³⁺ and is pumped by the perovskite host. The excitation and emission spectra of CsPbBr₃, Yb³⁺-doped CsPbBr₃, and SiO₂-encapsulated Yb³⁺-doped CsPbBr₃ NCs are shown in Fig. 16(a). The energy transfer process from the CsPbBr₃ to the Yb³⁺ ion is shown in Fig. 16(b).

The synthesized Yb³⁺-doped CsPbBr₃ NCs emits strong NIR emission. The emission peak is centered at 985 nm. This originated from the ²F_{5/2} → ²F_{7/2} transition in Yb³⁺ ions. The intrinsic transition in Yb³⁺ ions is excited by efficient energy transfer from the perovskite host. Since there is a charge difference between Yb³⁺ and Pb²⁺, the charge compensation defects V_{Pb} were generated.^{73,190} The V_{Pb} exists between the two Yb³⁺ ions in the form of Yb³⁺-V_{Pb}-Yb³⁺. The V_{Pb} can excite two Yb³⁺ ions nearby through the quantum-cutting process and thus a high PL quantum yield is obtained.^{191,192} The Yb³⁺-doped CsPbCl₃ NCs emits 986 nm NIR light from the ²F_{5/2} → ²F_{7/2} transition, whereas Yb³⁺/Er³⁺ co-doped CsPbCl₃ NCs emits

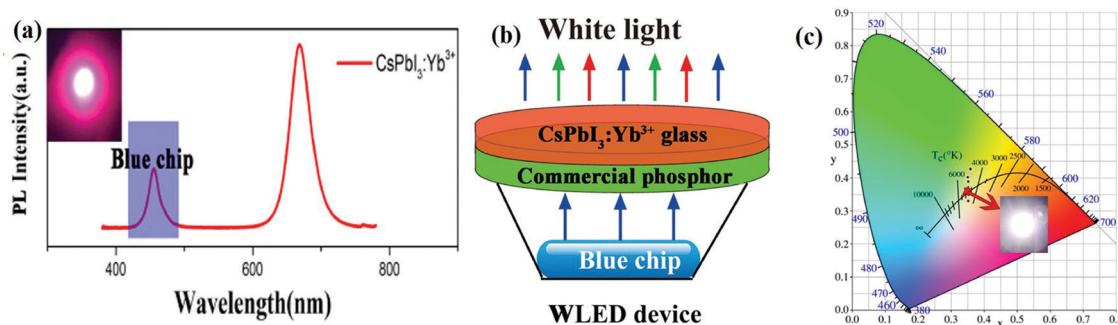


Fig. 15 (a) PL spectrum of Yb³⁺-doped CsPbI₃ NCs integrated with the GaN blue chip. (b) Schematic of the device structure for WLEDs. (c) The color coordinates of the WLEDs (0.3499, 0.3542). Reproduced with permission from ref. 185. Copyright ©2020, Elsevier.

Table 10 The lanthanide-doped CsPbX₃ WLEDs parameters

Ln-Doped WLED structure	CIE coordinates	LE (lm W ⁻¹)	CRI	CCT (K)	NTSC (%)	Year
Nd:CsPbBr ₃ + CsPbBr ₃ + CsPbBr _{1.2} I _{1.8} /PMMA film	(0.34, 0.33)	—	—	—	122.0	2020 ¹⁸⁹
Dy:CsPbBr ₃ + Mn:K ₂ SiF ₆ + InGaN LED chip	(0.2881, 0.3001)	—	—	—	126.3	2022 ¹⁸⁴
Yb:CsPbI ₃ + Ce:Y ₃ Al ₅ O ₁₂ + GaN LED chip	(0.3499, 0.3542)	57.3	85.4	3524	—	2020 ¹⁸⁵
Ce:Eu:CsPbCl ₃ + polystyrene + GaN LED chip	—	23	73	—	—	2018 ¹⁸²
Ce:Eu:CsPbCl _{1.8} Br _{1.2} + polystyrene + GaN LED chip	—	36	92	—	—	2018 ¹⁸²
Ce:Sm:CsPbCl ₃ + polystyrene + GaN LED chip	—	15	70	—	—	2018 ¹⁸²
Ce:Sm:CsPbCl _{1.8} Br _{1.2} + polystyrene + GaN LED chip	—	27	84	—	—	2018 ¹⁸²

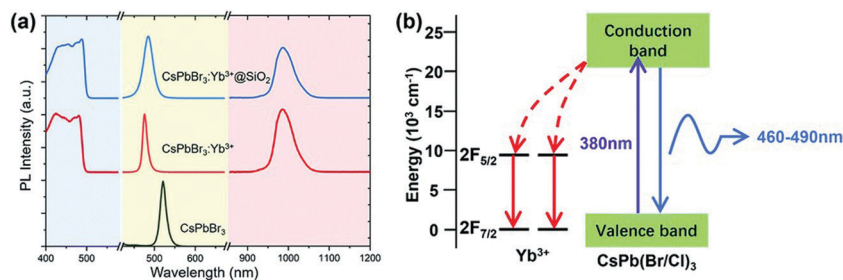


Fig. 16 (a) Excitation spectra (emission 985 nm, left), visible PL spectra (middle), and infrared PL spectra (right) of the synthesized CsPbBr₃, Yb³⁺-doped CsPbBr₃, and SiO₂-encapsulated Yb³⁺-doped CsPbBr₃ NCs. (b) Schematic diagram of energy transfer in the Yb³⁺-doped CsPbBr₃ NCs. Reproduced with permission from ref. 190. Copyright©2020, Royal Society of Chemistry.

NIR emission centered at 1533 nm for the transition from $^4I_{13/2} \rightarrow ^4I_{15/2}$ of Er³⁺ ions.¹⁷⁴ Zeng *et al.*¹⁹³ reported various strategies to enhance the NIR emission by doping lanthanide ions into the CsPbCl₃ NCs. It was observed that Er³⁺, Ho³⁺, and Nd³⁺ doping into CsPbCl₃ NCs can emit intense NIR light through energy transfer mediated by Mn²⁺ ions. The emission wavelength centered at 1542 nm was observed for Er³⁺ *via* a transition from $^4I_{13/2} \rightarrow ^4I_{15/2}$. In Ho³⁺, the transition takes place from $^5F_5 \rightarrow ^5I_7$ and $^5F_5 \rightarrow ^5I_6$ and corresponding emission peaks are observed at 986 nm and 1484 nm, respectively. In the case of Nd³⁺ ions, three emission peaks were observed which were centered at 888 nm, 1064 nm, and 1339 nm corresponding to $^4F_{3/2} \rightarrow ^4I_{9/2}$, $^4F_{3/2} \rightarrow ^4I_{11/2}$, and $^4F_{3/2} \rightarrow ^4I_{13/2}$ transitions, respectively. Lanthanide-doped all-IHPs NIR emission transitions and their peak wavelengths are listed in Table 11.

NIR-LEDs are useful in night vision cameras, bio-imaging, communications and food processing industries. Huang *et al.*¹⁷³ proposed NIR-LEDs by doping ytterbium into CsPbCl₃. The emission and absorption spectra of CsPbCl₃ NCs and Yb³⁺ ion-doped CsPbCl₃ NCs are shown in Fig. 17. The emission of Yb³⁺ ions at ~1000 nm is suitable for NIR-LEDs. Fig. 18 demonstrates the application of Yb³⁺-doped CsPbCl₃ as a NIR camera. The device shows an output irradiance of 112 mW cm⁻²@400 mA with

excellent stability. For the analysis of Yb³⁺-doped CsPbCl₃ as a NIR camera, photographs of fruits and a fist were taken in natural light and phosphor-converted NIR-LED light. When the NIR-LED is off, the fruits and fist are invisible to the eye, whereas when the NIR-LED is on, the black and white images of the fruits and fist are observed. The images recorded under natural light phosphor-converted Yb³⁺-doped CsPbCl₃ NIR-LED light are shown in Fig. 18(a) and (b), respectively.

3.2.4.4 Emerging applications for optical temperature sensing.

In addition to the optoelectronic device applications, lanthanide-doped all-IHPs have recently been explored for various types of sensing applications. In recent years, temperature-dependent PL spectra have been studied widely in lanthanide-doped materials. Lanthanide-doped all-IHPs showed a linear variation in PL peak intensity with a temperature variation. This characteristic of Ln³⁺-doped all-IHPs has attracted the attention of researchers for non-contact-based temperature sensing applications. In lanthanides and transition metals, the PL intensity variation occurs due to the electron population in the thermally coupled states.¹⁹⁴ However, a very small energy gap between these thermally coupled states leads to the overlapping of the emission. This affects the

Table 11 NIR emission in lanthanide-doped inorganic halide perovskites

Lanthanide-doped CsPbX ₃	Transition	NIR emission peaks (nm)
Yb ³⁺ -CsPbBr ₃ NCs	$^2F_{5/2} \rightarrow ^2F_{7/2}$	976, ¹⁷³ 985, ¹⁹⁰ 986 ¹⁷⁴
Yb ³⁺ /Er ³⁺ -CsPbBr ₃ NCs	$^4I_{13/2} \rightarrow ^4I_{15/2}$ (Er ³⁺)	1533 ¹⁷⁴
Er ³⁺ -CsPbCl ₃ NCs	$^4I_{13/2} \rightarrow ^4I_{15/2}$	1542 ¹⁹³
Ho ³⁺ -CsPbCl ₃ NCs	$^5F_5 \rightarrow ^5I_7$, $^5F_5 \rightarrow ^5I_6$	986, 1484 ¹⁹³
Nd ³⁺ -CsPbCl ₃ NCs	$^4F_{3/2} \rightarrow ^4I_{9/2}$, $^4F_{3/2} \rightarrow ^4I_{11/2}$, $^4F_{3/2} \rightarrow ^4I_{13/2}$	888, 1064, 1339 ¹⁹³
Yb ³⁺ -CsPbI ₃ QDs	$^2F_{5/2} \rightarrow ^2F_{7/2}$	988 ¹⁸⁵

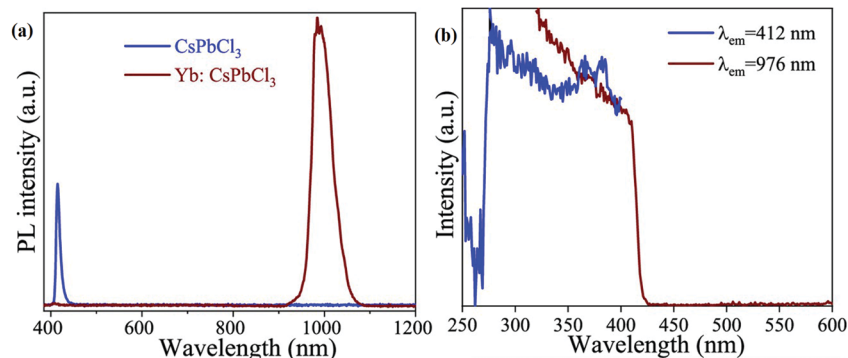


Fig. 17 (a) Emission and absorption spectra of CsPbCl₃ NCs and Yb³⁺-doped CsPbCl₃ NCs. (b) Excitation spectra of CsPbCl₃ NCs and Yb³⁺-doped CsPbCl₃ NCs. Reproduced with permission from ref. 173. Copyright©2021, American Chemical Society.

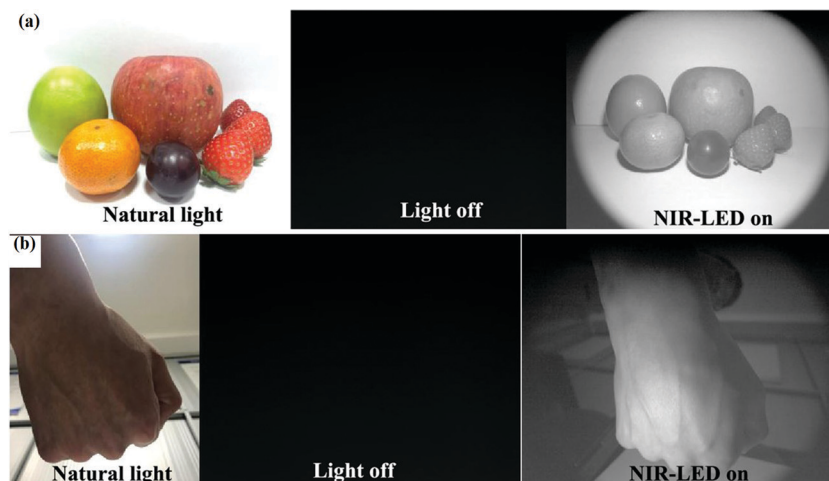


Fig. 18 Images of fruits and a fist under natural light and NIR-LEDs light were recorded using a visible and NIR camera, respectively. Reproduced with permission from ref. 173. Copyright©2021, American Chemical Society.

temperature sensing accuracy. With an increase in temperature, the electron–phonon coupling becomes more and more prominent and leads to the thermal quenching of the PL intensity.

Zhang *et al.*¹⁹⁵ demonstrated the application of Tb³⁺-doped CsPbI₃ NCs for optical temperature sensing. The temperature-dependent emission spectra of Tb³⁺-doped CsPbI₃ NCs are shown in Fig. 19(a). As the temperature increases, the emission intensities of both the Tb³⁺ ions and CsPbI₃ NCs decrease systematically. Fig. 19(b) shows the integrated emission intensities corresponding to Tb³⁺ and CsPbI₃ emission in Tb³⁺-doped CsPbI₃ NCs at various temperatures. The fluorescence intensity ratio of Tb³⁺ at 544 nm and CsPbI₃ at 677 nm with excitation at 480 nm is given by the following:

$$\text{FIR} = \frac{I_{\text{Tb}}}{I_{\text{CPI}}} = \frac{I_{0,\text{Tb}}}{I_{0,\text{CPI}}} \frac{1 + A_{\text{CPI}} \exp\left(\frac{-E_{\text{CPI}}}{k_{\text{B}}T}\right)}{1 + A_{\text{Tb}} \exp\left(\frac{-E_{\text{Tb}}}{k_{\text{B}}T}\right)} \approx B + C \exp\left(\frac{-\Delta E}{k_{\text{B}}T}\right) \quad (5)$$

where I and I_0 are the PL intensities at temperature T and 0 K, respectively; A is a pre-exponential constant, T is the absolute temperature, the quenching activation energy is represented by E , and k_{B} is the Boltzmann constant. In the above equation, B , C and E are the values related to I_0 , A and E , respectively.

The absolute sensitivity is defined as $S_{\text{A}} = \frac{\partial \text{FIR}}{\partial T}$, and the relative sensitivity is $S_{\text{R}} = \left| \frac{1}{\text{FIR}} \frac{\partial \text{FIR}}{\partial T} \right| \times 100\%$. The FIR value was calculated for the temperature range 80–480 K. The maximum reported values of S_{A} and S_{R} are 0.034 K⁻¹ and 1.78% K⁻¹ as shown in Fig. 19(c). The reversible effect on the FIR with temperature was also determined. The FIR remained almost the same in the cyclic temperature process as shown in Fig. 19(d). Yao *et al.*¹⁹⁶ also reported Dy:CsPbBr₃ QDs as a temperature sensor in the temperature range 80–298 K. For optimized Dy³⁺ doping, the Dy:CsPbBr₃ QDs showed the maximum relative sensitivity 2.39% K⁻¹ at 298 K.

Table 12 summarizes the LED parameters of lanthanide-doped all-IHPs. Yb³⁺-doped CsPbCl₃ showed a maximum S_{R} of 3.31 K⁻¹, whereas the wide temperature range response of 80–480 K was observed in Tb³⁺-doped CsPbCl₃. Therefore, one

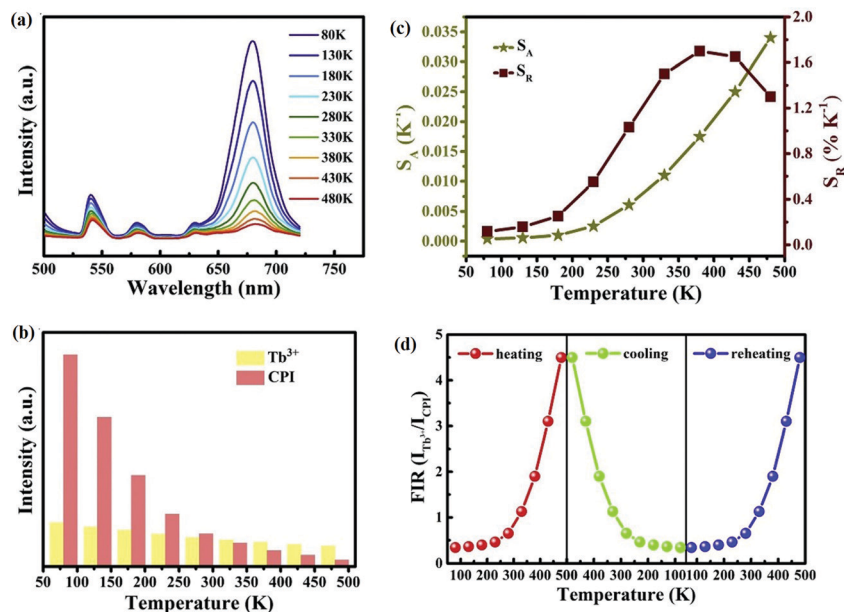


Fig. 19 (a) Temperature-dependent emission spectra of Tb³⁺-doped CsPbI₃ NCs excited at 480 nm. (b) Integrated emission intensities corresponding to Tb³⁺ and CsPbI₃ emission in Tb³⁺-doped CsPbI₃ NCs at various temperatures. (c) Absolute sensitivity S_A and relative sensitivity S_R versus T . (d) FIR in cyclic heating cooling and reheating. Reproduced with permission from ref. 195. Copyright © 2020, Journal of European Ceramic Society.

Table 12 The thermometric parameters of Ln³⁺-doped CsPbX₃ in temperature sensing

Ln ³⁺ :CsPbX ₃	Temperature range (K)	Maximum S_R (% K ⁻¹)	Maximum S_A (K ⁻¹)	Year
Tb:CsPbI ₃ NCs	80–480	1.78	0.034	2020 ¹⁹⁵
Dy:CsPbBr ₃ QDs	80–298	2.39	—	2021 ¹⁹⁶
Eu:CsPbCl ₂ Br ₁ QDs	80–440	3.097	0.0315	2021 ¹⁹⁷
Eu:CsPbBr ₃ QDs	93–383	2.25	0.0224	2020 ¹⁹⁴
Yb:CsPbCl ₃	80–300	3.31	—	2021 ⁷³

may select the particular combination of host and dopant to achieve the requirements under study. These open up future applications for fluorescence intensity ratio-based non-contact efficient temperature sensing. Hence, Ln³⁺ ion-doped CsPbX₃ shows prominent temperature sensitivity, which makes it a good candidate for temperature sensing applications.

3.2.4.5 Emerging application in optical encoding. In recent years, optical encoding research has become one of the most important fields of research in the scientific and technical industry for detecting counterfeiting. The poor materials, as well as their encoding in anti-counterfeiting technology, are easily depicted by the falsifier. It has been observed that stimuli-responsive fluorescence materials, such as lanthanide-doped all-IHPs, are very effective for optical data security with high recording density. Also, the fluorescence transitions switch between different states based on external factors such as temperature, dopant ions and their concentration, *etc.* Feng *et al.*¹⁹⁸ reported a novel approach to modeling optical encoding materials using europium complex-decorated CsPbBr₃ quantum dots with highly stable dual-stimuli-response. The schematic illustration of the formation of the europium complex Eu(PBA)₃AA (HPBA = *N*-(2pyridinyl)benzoylacetamide,

AA = 8-aminooctanoic acid)-decorated CsPbBr₃ quantum dots is shown in Fig. 20(a and b). The temperature and pH responses by the CsPbBr₃ (QDs) and Eu(PBA)₃AA, respectively, were observed in the luminescence spectra. This is useful for this application also. The encryption and decryption mechanisms are shown in Fig. 20(c) and (d), which show the dual responsive optical recording and encryption of the designed material.

OA/OAM-based QDs were painted on transfer paper and an encrypted word “LZU” was printed with Eu(PBA)₃AA-QDs, which was decoded only when the fluorescence of Eu(PBA)₃AA was enhanced by NH₃ vapor stimulation and the fluorescence of CsPbBr₃ was decreased by increasing the temperature to 80 °C as indicated in Fig. 20(d). The information “LZU” was doubly encrypted by temperature and pH and was readable only when these two values fulfilled the decryption conditions. Optical encryption and decryption were also reported by using Lu³⁺-doped CsPbBr₃ but decryption occurred in UV light instead of NIR light.¹⁷⁷ The information “ZJU” was encrypted using the blue-emitting ink of Lu³⁺:CsPbBr₃ on white paper. It is not possible to decode the information “ZJU” under daylight; however, when it encounters UV light of wavelength 360 nm, decryption of the information takes place. Hence, europium complex-decorated CsPbBr₃ quantum dots can be used as an optical encoding material in the future.

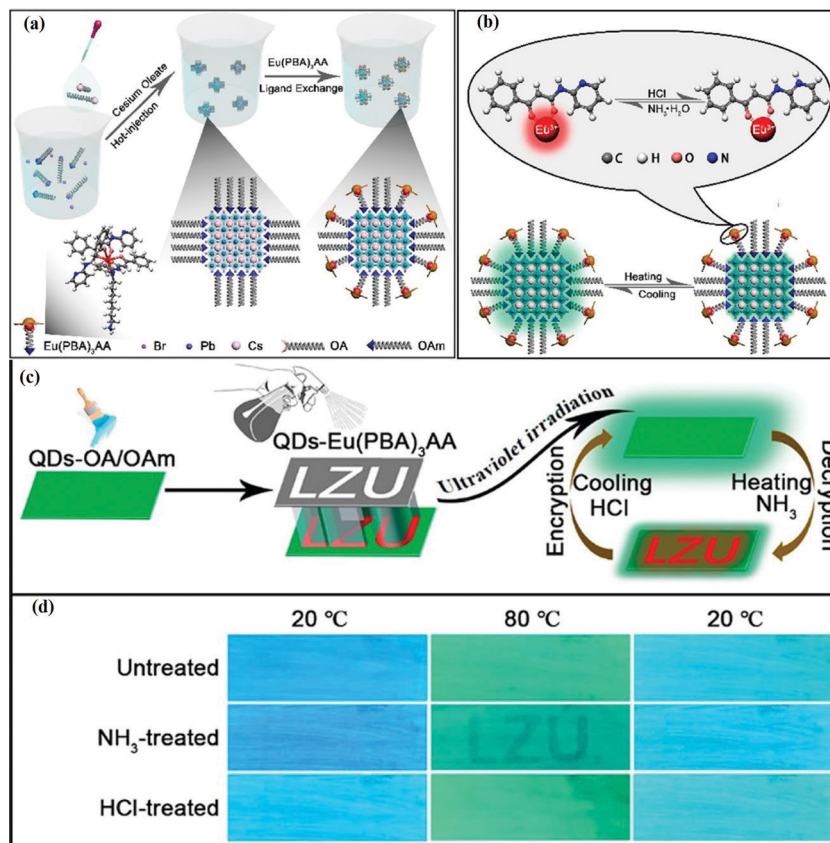


Fig. 20 (a) Schematic illustration of the formation of QDs-Eu(PBA)₃AA. (b) PL images of the dual-responsive optical recording and encryption. (c) The pattern design process and encryption and decryption mechanism. (d) PL images of patterns at different temperatures and pH. Reproduced with permission from ref. 198. Copyright©2021, American Chemical Society.

4. Summary and perspectives

The all-IHPs dominate organic-inorganic halide perovskites due to their better environmental stability, thus making them good candidates for optoelectronic applications. Conventionally, solid-state and liquid reaction synthesis methods have been used for the synthesis of bulk and nano-structured halide perovskites. Recently, researchers have reported several new synthesis techniques such as inject printing, spin coating, RF magnetron sputtering, single/multi crucible vacuum thermal evaporation, hot injection, *etc.* All these techniques have their advantages and disadvantages. Among these, the hot injection method is the most widely used method for the synthesis of all IHPs nanostructures with better stability. These reported synthesis methods are aimed toward the improved and stable structure of IHPs but none claim a completely stable phase synthesis. Therefore, the synthesis of cost-effective IHPs with long-term stability is still among the most challenging areas of research for IHPs.

In general, three phases (α , β , and γ) are observed in all-IHPs except in the perovskites formed by the halide I-atom, where an additional non-perovskite δ phase occurs. The cubic phase with a Goldschmidt tolerance factor value of 1 is the most stable structure. The stability can be increased by tailoring the Goldschmidt tolerance factor value by using surfactants and dopant

ions. One of the widely used dopants for IHPs is the lanthanide ion. The doping with lanthanide ions increases the stability (thermal stability, photostability, and phase stability) by reducing vacancies (defects and trap-states) in the structure and also improves optical properties. However, there is still a lot of scope for further improving the stability aspect of IHPs. A few front-line perspectives related to phase and stability issues can be outlined as follows. (i) Four phases are observed in all I-ion based IHPs. On heating, a direct transition from the α to δ phase occurs. However, in the cooling process, all four α , β , γ , and δ phases are observed. Herein, the reason for the direct transition from α to δ phase is not well addressed and needs further attention. (ii) Phase kinetics depends on both temperature and pressure. However, the study of applied pressure-based phase transition is not well explored in pristine and lanthanide-doped all-IHPs. (iii) In CsPbX₃, the toxicity of the Pb is unavoidable. Lead-free all-IHPs like CsGeX₃, CsGnX₃, *etc.*, are reported but their phase stability is quite low as compared to CsPbX₃. Replacing Pb²⁺ with any non-toxic cation considerably improves the stability and can open up an eco-friendly IHPs field. (iv) The development of single-crystal IHPs has not been tried so far. The single-crystal form of IHPs may also add new properties and should be explored in the future.

The all-IHPs provide a wide color gamut of emission spectra ranging from 400 nm to 700 nm by the compositional

management of halide ions. The FWHM of the emission peaks at 400 nm for CsPbCl₃ and 700 nm for CsPbI₃ ranges between 12 nm to 42 nm, respectively. The bandgap of the structure can be tailored from ~1.7 eV for CsPbI₃ to ~3.0 eV for CsPbCl₃. The doping of lanthanide ions in IHPs bestows them with excellent optical properties. It not only adds unique 4f–4f luminescence of lanthanide ions but affects the characteristic optical features of IHPs. The substitution of smaller-sized lanthanide ions (all lanthanide after Gd³⁺) in place of Pb²⁺ ion leads to lattice shrinkage. This causes an increased ligand field within the [PbBr₆]⁴⁻ octahedra, leading to an increase in the bandgap, and a blue shift in the PL is observed. Further, the emission intensity of the band-to-band transition of the host initially increases on increasing the lanthanide concentration because of the improved defect state, but after a certain limit, it starts decreasing due to FRET from the host to the doped lanthanide ion. Time-resolved spectroscopy reveals that the lanthanide-doped CsPbX₃ has a longer average lifetime and improved quantum yield as compared to the pristine CsPbX₃. In general, the average lifetime increases towards the higher atomic number of lanthanide ions. Longer average lifetimes, as well as increased PL quantum yields, are the consequences of the partial elimination of nonradiative channels in the lanthanide-doped CsPbX₃.

Anisotropic studies of Young's moduli of CsPbI₃, CsPbBr₂I, CsPbBr₂I and CsPbBr₃ structures have been reported. Young's moduli of CsPbI₃ and CsPbBr₃ along different directions are the same, whereas CsPbBr₂I showed isotropic nature along the [001] and [010] directions, and CsPbBr₂I along the [100] and [010] directions. The anisotropic behaviors of CsPbBr₂I and CsPbBr₂I are reflected in almost all transport properties, except for bandgap energy. Although the anisotropy exists along the [001] and [100] directions for CsPbBr₂I and CsPbBr₂I, respectively, the transport properties (electron and hole mobilities) are superior along [001] in both structures. In this direction, fewer carriers can be captured by the traps during transport. The superior properties of the crystal with the [001] orientation would be helpful in small devices for efficient output, such as transistors, light-emitting diodes, photodetectors, solar cells, *etc.* The extinction coefficients of CsPbBr₂I and CsPbBr₂I along the [001] direction are also greater as compared to [100] direction. Therefore, photon absorption along the [001] direction is greater and results in large current density and better spectral responsibility, which are required in optoelectronic applications. Thus, the anisotropic response for different parameters under applications is the extended field for making the device compact and with high efficiency. The effect of lanthanides on this property has not been explored so far.

Although optical properties have been widely explored, a few challenges remain. A theoretical understanding of various phenomena, such as phonon energy and its effect on optoelectronic properties and phase transition, the effect of temperature on PL spectra, in-depth study on doping ion behavior, *etc.*, is still lacking and needs to be addressed. Similarly, the tuning of the emission peak width with narrow FWHM is also one of the important ignored aspects. Narrow-band emitting IHPs can be used for switching and lasing applications. In addition to

this, lanthanide-doped IHPs can give multi-modal emission: downconversion, UC, and quantum-cutting luminescence. Such multimodal emission has not been explored well in IHPs. This multi-modal emission can be achieved by incorporating lanthanide-based phosphors/organic complexes in combination with the IHPs. This facilitates FRET pair formation between the duo, which opens up applications for biomedical imaging and sensing. However, such biological applications require lead-free and stable lanthanide-doped inorganic perovskites.

Due to the outstanding optoelectronic properties of all IHPs, they have attracted attention in several application areas like solar cells, colored LEDs, display devices, spectro-chemical probes, explosive detectors, laser fabrication, X-ray detection, *etc.* However, lanthanide doping has further extended its application fields and is additionally being used for WLEDs, NIR light emitters, NIR-LEDs, NIR cameras, temperature sensors, optical encoding, *etc.* For example, Er³⁺/Ho³⁺/Nd³⁺-doping into CsPbCl₃ NCs gives intense NIR light through mediated energy transfer by Mn²⁺ ions. The IR emission centered at 1542 nm was observed with Er³⁺ doping. The doping of Ho³⁺ ions gave emission peaks at 986 nm and 1484 nm. Due to the doping of Nd³⁺ ions, three emission peaks were observed at 888 nm, 1064 nm, and 1339 nm. Similarly, the NIR emission at 980 nm from Yb³⁺-doped CsPbCl₃ has been used for the development of NIR cameras, which could be useful in night vision surveillance, bio-imaging, communication and food processing industries, *etc.* In another application, Tb³⁺ ion-doped CsPbI₃ showed high-temperature sensitivity in the temperature range 80–480 K with the maximum values of absolute sensitivity (S_A) and relative sensitivity (S_R) 0.034 K⁻¹ and 1.78% K⁻¹, respectively. Similarly, Eu complex-decorated CsPbBr₃ quantum dots have been used as an optical encoding material that has the potential for optical data storage and readout and anti-counterfeiting applications.

In conclusion, lanthanide doping not only improves the stability and optical properties of IHPs but also brings multi-functionality to them, beyond the well-established solar cell applications. Lanthanide-doped inorganic perovskites have great potential, and better theoretical and experimental studies may open up plenty of new application areas for them.

Conflicts of interest

There are no conflicts to declare.

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