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# 6

## Sensitization of $\text{Yb}^{3+}$ using $\text{CsPbBr}_x\text{Cl}_{3-x}$ nanocrystals

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*Lead halide perovskite nanocrystals have been widely studied in recent years due to their huge application potential as a cost-effective UV-VIS semiconductor. In this work we prepare and study  $\text{Yb}^{3+}$ -doped all-inorganic perovskite nanocrystals. Introduction of rare earth (RE) ions is a popular way to modify photonic properties of materials, due to their sharp, temperature stable, and host-independent, electronic transitions in VIS-NIR. Yet, owing to their small absorption cross-sections, for practical applications of RE-doped materials, there is an urgent need for efficient sensitization; that is a host-mediated energy transfer process that effectively enhances the excitation cross-section of the RE ions. Perovskites are a natural candidate to host RE dopants, providing strong absorption and high tolerance to crystal defects. Here we explore  $\text{Yb}^{3+}$ -doped  $\text{CsPbX}_3$  perovskite NCs, characterizing them by their optical properties. In particular, we explore the NIR photoluminescence, and discuss the excitation mechanism of  $\text{Yb}^{3+}$  ions, their photoluminescence quantum yield and its limits. Lastly, the importance of the perovskite composition is explored, in which chloride in the host perovskite, plays an important role. Keeping in mind applications such as down-conversion layers for solar cells, the potential for device development of these  $\text{Yb}^{3+}$  doped perovskites looks very promising.*

## 6.1 Introduction

Featuring 980 nm emission,  $\text{Yb}^{3+}$ -doped materials are applied in short-wave infrared lasers and in combination with other rare earth (RE) ions to form up- and down-converting pairs. Specifically, they are applied in solid state lasers, and double clad fiber lasers, as the emitter in the active gain material. The emission arises from a single transition between  $J$  states of the incomplete 4f electron shell of trivalent ytterbium ion ( $\text{Yb}^{3+}$ ). More specifically, the transition from the excited  $^2\text{F}_{5/2}$  to the ground state,  $^2\text{F}_{7/2}$ . [121, 122] Due to the effective screening of the 4f shell by the complete outer 5s and 5p orbitals, the host has only a very limited influence on the energy structure of the  $\text{Yb}^{3+}$  ions; consequently a narrow emission band with a temperature invariant wavelength can be observed up to room temperature. [123] However, transitions between the individual  $J$  states are only weakly allowed, yielding very long radiative lifetimes ( $\approx$  ms) and very small optical absorption cross-sections.

While the host materials do not influence the emission wavelength, they are of importance as they can act as sensitizers for the excitation of the  $\text{Yb}^{3+}$  ions. Sensitization proceeds through energy transfer from the host carriers to the ion, promoting an excitation of the  $\text{Yb}^{3+}$  ion. In order to take place, this places clear requirements on both the energy states of the host, as well as the localization of the carrier in the vicinity of the ion. [8] This is more easily accomplished by exploiting defect states, and is observed in the sensitization process of other REs systems as well, such as Eu:GaN shown in chapter 4 and Er:SiNCs shown in chapter 5.

The host materials explored here is cesium lead halide ( $\text{CsPbX}_3$ ) perovskite nanocrystals (NCs), a novel semiconductor material with strongly tunable bandgap energy. The easy and relatively low temperature synthesis, combined with the complex crystal structure typically results in a high defect density in most other semiconductors. But in the case of lead halide perovskites, the optical properties as well as carrier mobilities seem to be unaffected; ergo perovskites are highly defect tolerant. Moreover, the perovskite crystal structure is very tolerant to lattice distortions, in that way facilitating doping.

Evidence to the acceptance of dopants into the perovskite lattice are several works, including lanthanides, [124, 125] manganese, [126, 127] and several metals. [128] Strong  $\text{Yb}^{3+}$  emission has been shown to occur from  $\text{Yb}^{3+}$  doped  $\text{CsPbCl}_3$  perovskites, [125] as well as  $\text{CsPbBr}_3\text{Cl}_{3-x}$ . [124] With efficient quantum cutting properties, a photoluminescence quantum yield (PLQY) of  $\text{Yb}^{3+}$  emission of up to 190% has been shown, [129] therefore this material is highly interesting, with possible PV applications, such as solar concentrators [130], or spectral shapers [124].

Here, we make use of the procedures shown in Pan *et al.*, [125] to successfully synthesize  $\text{Yb}^{3+}$  doped  $\text{CsPbCl}_3$  perovskite NCs. The excitation mechanism of  $\text{Yb}^{3+}$

and the importance of the perovskite composition are explored. While at first it seems that the composition plays an important role only for the compatibility of  $\text{Yb}^{3+}$  in the perovskite lattice, we also explore the implications the composition has on the energy structure of the  $\text{Yb}:\text{CsPbX}_3$  system.

### 6.1.1 Experimental details

#### Sample preparation

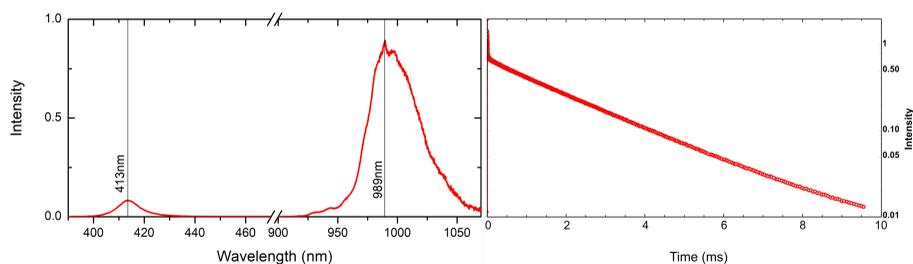
$\text{Yb}:\text{CsPbCl}_3$  nanocrystals in colloidal dispersion were synthesized via a modified version of the hot-injection protocol described by Pan *et al.* [125], and the full synthesis details were published elsewhere. [131] After synthesis the samples were purified according to the protocol and eventually stored in 3.5 mL quartz cuvettes. For halide-exchange three different salts were used:  $\text{PbBr}_2$  (Sigma-Aldrich,  $\text{PbCl}_2$  98%),  $\text{PbBr}_2$  (Sigma-Aldrich,  $\text{PbCl}_2$  98%), and  $\text{YbBr}_3$  (Sigma-Aldrich,  $\text{PbCl}_2$  99.99% anhydrous).

#### Optical characterization

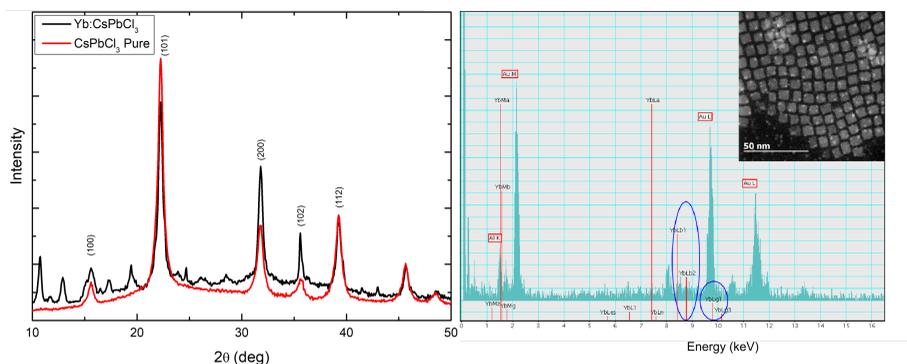
For time-resolved measurements an optical parametric oscillator (OPO) pumped by the third harmonic of a 100 Hz Nd:YAG laser, with a pulse duration of 5 ns was used. Emission was dispersed by an M266 (Solar LS) monochromator coupled to a NIR photo multiplier tube (Hamamatsu) for photon detection. For spectral measurements such as PL and PLE spectra, a Fluorolog-3 (HORIBA Jobin Yvon) spectrometer was used, employing a Xenon lamp coupled to a monochromator as an excitation source, coupled to detection monochromator with Si CCD (Synapse). To investigate PLQY an integrating sphere was used (Newport, 7.5 cm diameter), with excitation source a xenon lamp (L2273 Hamamatsu) coupled to a double grating monochromator (Solar MSA130). Due to the wide detection range necessary with excitation and emission in the UV and NIR (280 nm to 1050 nm), respectively, the spectral response was calibrated using a Newport tungsten-halogen and deuterium-arc calibration lamp.

## 6.2 Results

Several different mechanisms were explored for the incorporation of  $\text{Yb}^{3+}$  inside  $\text{CsPbX}_3$  perovskite crystals. And while the linear absorption signal of  $\text{Yb}^{3+}$  could be observed in some of the synthesized materials, the sensitization of  $\text{Yb}^{3+}$  emission remained elusive. [131] The material studied here is developed the synthesis as described in 6.1.1, following the work of [124, 125]. Notably, while in much of the perovskite studies, bromide based LHP, show the brightest and most stable PL, the chloride based LHP (in contrast to bromide) seem to be the most successful  $\text{Yb}^{3+}$  host for  $\text{Yb}^{3+}$  doping. In this study we focus only on those samples in which  $\text{Yb}^{3+}$  was successfully sensitized by  $\text{CsPbX}_3$  and was optically active, while other samples



**Figure 6.1:** Photoluminescence **Left**, PL spectrum of an  $\text{Yb}^{3+}$  doped  $\text{CsPbCl}_3$  sample, showing two emission peaks. **Right**, time resolved PL transient, of the  $\text{Yb}^{3+}$  emission (detection at  $\lambda = 980$  nm), can be fitted with a 2.0 ms exponential decay.



**Figure 6.2:** Crystal characterization **Left**, XRD pattern of doped and undoped  $\text{CsPbCl}_3$  perovskites. The crystallographic patterns are unaltered by doping, extra peaks appear due to organic synthesis byproducts. **Right**, EDS spectrum of a selection of doped NCs as shown in the inset. No  $\text{Yb}^{3+}$  lines are visible.

were discussed in depth in [131].

In Fig. 6.1 the PL spectrum of a studied sample is shown. Two emission peaks can be observed: the perovskite excitonic emission peak at,  $\sim 415$  nm, and the IR peak originating from the  ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$  transition of the  $\text{Yb}^{3+}$ , peaking at  $\sim 988$  nm. While the  $\text{Yb}^{3+}$  peak, originates from a single atomic transition, it has considerable broadening. This is not uncommon for RE-doped materials, and is attributed to local crystal-field fluctuation. [121] The TRPL transient shown in Fig. 6.1, can be fitted with an exponential decay. The perovskite emission (not shown) has a short lifetimes of approx.  $\sim 5$  ns, while the  $\text{Yb}^{3+}$  emission has a very long lifetime of  $1.96 \pm 0.01$  ms. The uniquely long  $\text{Yb}^{3+}$  lifetime is another confirmation that the  $\sim 988$  nm peak is in fact due to the forbidden  ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$  transition.

In Fig. 6.2 the TEM and XRD spectra of the studied sample are shown. The observed NCs were confirmed by XRD to have a crystalline perovskite structure. The peak positions and width could indicate whether modification of the crystal lattice has taken place in order to accommodate the dopant within the structure. From our observation, the lattice appears unperturbed compared to the undoped CsPbCl<sub>3</sub> samples. This is in contrast to Ref. [125] where a clear lattice modification is observed, depending on the used lanthanide. Extra peaks in the XRD spectrum are visible as well, which appear to result from residues of the synthesis process. The HRTEM, shows clusters which are different than the cubic perovskites. Elemental analysis (EDS) reveals that these are most probably YbO<sub>3</sub> inclusions. From both, the XRD, and EDS we cannot observe any signal from the incorporation of Yb into the perovskite crystals, and can only observe the signature of YbO<sub>3</sub> clusters separated from the NCs. We therefore conclude on two possibilities:

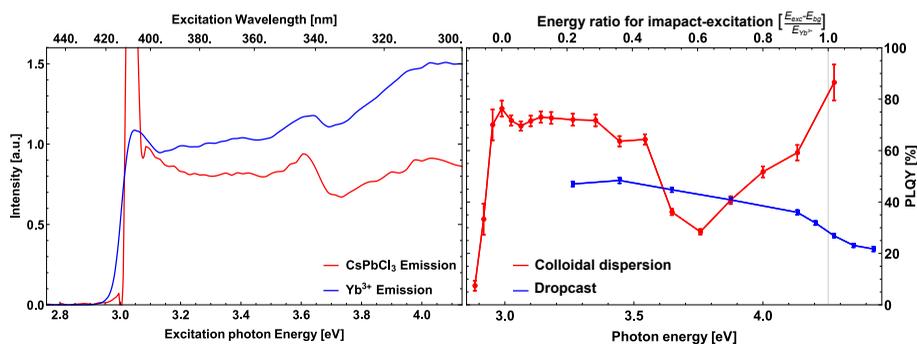
1. The CsPbX<sub>3</sub> perovskites NCs are *undoped*, and Yb<sup>3+</sup> emission originates from the oxide clusters.
2. The CsPbX<sub>3</sub> perovskites NCs are *doped* with Yb<sup>3+</sup>, but below the detection limit of the two techniques.

Possibly #1 implies that we have efficient transfer to the cluster, which contain emissive Yb<sup>3+</sup> ions. YbO<sub>3</sub> is considered an insulator with a bandgap energy of 4.6 eV, and if taking place then quantum confinement will make the bandgap grow, and not decrease in nanoform. [132] Considering we are not exciting with enough energy to excite the oxide phase, and the strong emission intensity of Yb<sup>3+</sup>, we can already speculate that the second option is the likelier conclusion, but this will be revisited later on.

## 6.3 Discussion

### 6.3.1 Excitation mechanism of ytterbium

Possibly the most important question pertinent to the investigated material is the role of perovskite NCs in sensitization of Yb<sup>3+</sup> emission. With so many elements involved, and the inherent instability of the perovskites, perhaps some specific compound clusters could have formed which excite the Yb<sup>3+</sup> ion. For this we explore the PL excitation (PLE) spectrum of the Yb<sup>3+</sup> as well as of perovskite in Fig. 6.3. The PLE gives the intensity of emission at a certain chosen detection wavelength, as a function of excitation wavelength. The PLE demonstrates that the excitation of Yb<sup>3+</sup> coincides with excitation of the perovskite: they both start emitting at excitation energies larger than the perovskite bandgap energy, and within the available experimental



**Figure 6.3: PLE and PLQY.** Left, PLE spectra of the  $\text{Yb}^{3+}$  peak and the perovskite peak. Both show similar features but vary in absolute value, the difference is ascribed to reabsorption and scattering of the PL. Right,  $\text{Yb}^{3+}$  PLQY of a toluene dispersed sample, and dropcast sample on a quartz substrate. The top axis, shows the reduced energy scale, in which above 1.0, there should be sufficient energy for impact excitation of another  $\text{Yb}^{3+}$  ion.

resolution show the same spectral shape. This tells us that excitation of the  $\text{Yb}^{3+}$  does proceed via optical excitation of the perovskite NCs.

Having shown that  $\text{Yb}^{3+}$  excitation proceeds through the perovskite NCs, we now consider the energy balance. The bandgap energy of the  $\text{CsPbCl}_3$  perovskite NCs used is 2.95 eV, while the single possible transition of  $\text{Yb}^{3+}$  has an energy of 1.26 eV. At every  $\text{Yb}^{3+}$  excitation event, the excess of energy,  $2.95 - 1.26 = 1.69$  eV, has to be dissipated. This gives two possibilities: either there is a non-radiative state, most probably in the perovskite NC which absorbs this excess energy, or an observed emitter, a second  $\text{Yb}^{3+}$  ion, is excited. From an application perspective, the latter is the most interesting option, and in the vast studies performed on LHP NCs, no indication of the first option has been found. In order to affirm one of the two statements we study the PLQY of the  $\text{Yb}^{3+}$  ions. If two  $\text{Yb}^{3+}$  ions *need* to be excited simultaneously, it would mean that for every absorbed photon by a perovskite NC, two photons from the  $\text{Yb}^{3+}$  ion are emitted. This implies that the PLQY of  $\text{Yb}^{3+}$  emission is double that of the undoped perovskite PL, and furthermore implies a PLQY that could go above unity. Though, it should be noted, a real world PLQY below unity, does not invalidate this possibility of two excited  $\text{Yb}^{3+}$  ions per perovskite, as not every perovskite is necessarily coupled to two  $\text{Yb}^{3+}$  ions.

The PLQY measurements shown in Fig. 6.3 give an maximum PLQY of  $\leq 1\%$  and  $\sim 75\%$  for the perovskite NCs and  $\text{Yb}^{3+}$  ions emission, respectively. An above unity PLQY would have proven beyond a doubt that sensitization proceeds using, and even requires, two  $\text{Yb}^{3+}$  ions. Considering we still observe perovskite emission, we can

argue that not all perovskites have been doped successfully. Furthermore, considering the more strict requirement of at least two ions per NC, it is clear that heavy doping is needed. Moreover, even in undoped LHP NCs, the PLQY is not unity, as sample stability and impurities can quench emission, and this might play a role in our samples. Nevertheless, in literature  $\text{Yb}^{3+}$  ion PLQYs of up to 190% are observed [125,129], we can therefore conclude that with sufficient sample optimization and sufficient doping concentration, above unity  $\text{Yb}^{3+}$  PLQYs is possible, and that two  $\text{Yb}^{3+}$  ions can indeed be excited per NC.

In our own attempts [131] at Yb doping of  $\text{CsPbBr}_3$ , no optical activity was observed. From the presented reasoning, we can already recognize at least one reason for that, which is the higher doping concentration necessary ( $\geq 2 \text{Yb}^{3+}$  ions per NC). However, another reason can also be recognized: that is the choice of halide in the perovskite NC. In most past attempts the focus was put on  $\text{CsPbBr}_3$ , having the highest stability and brightest emission of the LHP NCs. It is evident though that  $\text{CsPbBr}_3$  NCs with their smaller bandgap, do not have sufficient energy to excite two  $\text{Yb}^{3+}$  ions, and at least a mixed composition of  $\text{CsPbBr}_x\text{Cl}_{3-x}$  is needed. In the case of  $\text{CsPbBr}_3$  there is only sufficient energy to excite a single ion, with a large excess energy which needs to be compensated for (by defects or phonons) which considerably lowers the probability of the whole process.

The greater than unity PLQY observed in literature is a remarkable development, showing that these materials might be extremely interesting for down-conversion applications. Furthermore, we can conclude that the excitation mechanism plays a pivotal role in both the choice of doping concentration as well as in the choice of perovskite NC composition.

### 6.3.2 Efficient $\text{Yb}^{3+}$ sensitization

Having established that the excitation mechanism should allow excitation of two Yb ions per NC, we can now speculate further; can we excite more than two  $\text{Yb}^{3+}$  ions per NC. If we excite a NC above the bandgap the exciton will eventually relax (electron/hole to the edge of CB/VB, respectively), and excess energy is converted into heat. But before (or during) the exciton relaxation process, the exciton might have sufficient energy to excite an  $\text{Yb}^{3+}$  ion (or more), and afterwards proceed to normal excitation of two  $\text{Yb}^{3+}$  ions as discussed before. Here, this concept is explored further by use of excitation energy dependent PLQY measurements. If more than two  $\text{Yb}^{3+}$  ions can be excited, then above a specific excitation energy, we can expect an increase in  $\text{Yb}^{3+}$  PLQY, theoretically up to 300% for three  $\text{Yb}^{3+}$  ions. But considering the samples studied here do not display  $\text{PLQY} > 100\%$  we can assume that over  $> 200\%$  will not be observed either. Nevertheless, any increase in PLQY at excitation energies above the threshold energy, will be a very strong indicator of this effect, and will establish a second excitation path of  $\text{Yb}^{3+}$  – that of impact excitation.

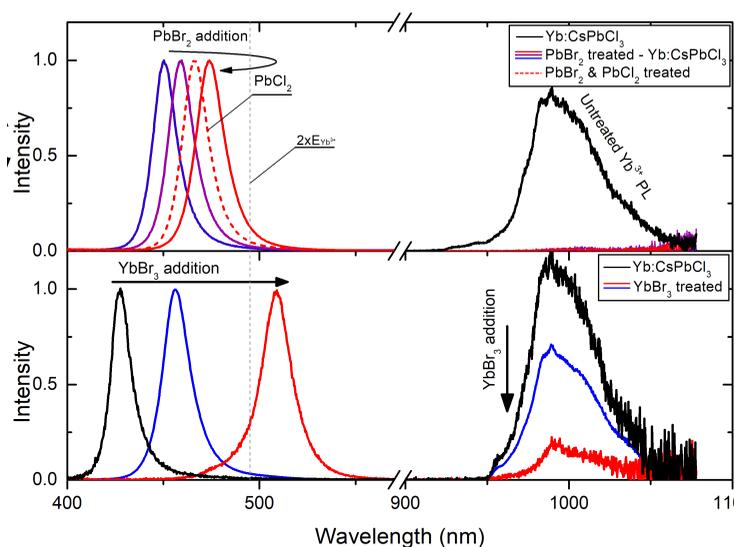
We perform PLQY measurements, and the PLQY is measured at the excitation range 3.2 eV to 4.43 eV. We assume that a relaxed band edge carrier excites two  $\text{Yb}^{3+}$  ions at a time, and therefore the excess energy for a third ion, has to be taken from the band edge energy. With a transition energy of  $E_{\text{Yb}^{3+}} = 1.26$  eV, we might observe the increase in PLQY, only when the excitation energy is above the perovskite PL bandgap energy,  $E_{bg}$ , with the additional  $\text{Yb}^{3+}$  transition energy,  $E_{\text{Yb}^{3+}}$ . This allows us to define a reduced energy scale,  $E_{\text{red}} = \frac{E_{\text{exc}} - E_{bg}}{E_{\text{Yb}^{3+}}}$ , with  $E_{\text{exc}}$  the excitation photon energy. We see that for  $\text{CsPbCl}_3$  with band gap energy,  $E_{bg} = 2.95$  eV, we need to excite above the threshold energy of 4.22 eV, which is problematic for the dispersion solvent used. In Fig. 6.3 we can observe an increase at higher energies, and can dismiss it as a result of the parasitic absorption from the solvent. To overcome this, the solvent is evaporated, and samples are prepared on a substrate, the PLQY of these is shown in Fig. 6.3. Here we observe no increase in PLQY as the excitation energy is increased beyond the impact-excitation threshold energy of 4.22 eV. Perhaps, 0.2 eV above the threshold energy, is not sufficient for excitation via this route, and a better alternative is changing sample composition and bandgap to lower  $E_{bg}$ , and thus the threshold energy.

It seems then, that in our measurements, we cannot observe a third  $\text{Yb}^{3+}$  ion, excited by the excess energy of highly excited perovskite NCs. A deeper look at literature might shed some light on why this is. Milstein *et al.* [133] show that transfer from perovskite to  $\text{Yb}^{3+}$  ion happens at extremely high rates, and is faster than their experimental resolution (150 fs). While the firstly discovered excitation mechanism of the two ions has not been established with certainty. According to their findings a shallow defect state is formed by the doped  $\text{Yb}^{3+}$  ions, and this state coincides with the excitation of two  $\text{Yb}^{3+}$  ions. If such a defect state can accommodate an excitation of a third ion, is unknown but presumably improbable. Alternatively, impact excitation could make use of the excess energy of the hot exciton to excite an additional ion, as studied in chapter 5 for Si NCs. After, the hot exciton impact-excites an  $\text{Yb}^{3+}$  ion, the NC is still excited at the band edges, and will have sufficient energy to excite two  $\text{Yb}^{3+}$  ions as usual. As of yet though, the excitation of the third ion, by either mechanism is not observed.

Lastly, we could speculate further and say that perhaps two of these defect states might accommodate four  $\text{Yb}^{3+}$  ions through the normal defect mediated transfer, so that excess energy might be utilized that way. Unfortunately, this requires excitation energies which are in the deep UV ( 250 nm) and is highly impractical.

### 6.3.3 Halide exchange

As we have discussed, the incorporation of chloride in the perovskite is of importance. The inclusion of chloride increases the bandgap energy, energetically facilitating the excitation of two  $\text{Yb}^{3+}$  ions per NC. In order to explore this more directly we



**Figure 6.4: Halide Exchange.** Emission spectra of  $\text{Yb}^{3+}$  doped  $\text{CsPbCl}_3$  perovskites, modified by halide exchange. **Top:** Halide exchange reveals excitonic red-shift with  $\text{PbBr}_2$  (purple to red), and subsequent blue-shift after halide exchange with  $\text{PbCl}_2$  (dashed), but regardless of NC excitonic bandgap, maintains strongly quenched  $\text{Yb}^{3+}$  emission compared to reference (black). **Bottom:**  $\text{YbBr}_3$  exchange reveals both a constant red-shift of perovskite peak as well as gradual quench in  $\text{Yb}^{3+}$  emission.

modified the perovskite NCs post-synthesis, by halide exchange. [134] Starting with  $\text{Yb}^{3+}$  doped  $\text{CsPbCl}_3$ , and gradually introducing bromide, we decrease the bandgap, while following the effect it has on  $\text{Yb}^{3+}$  sensitization.

In Fig. 6.4 the spectrum of  $\text{Yb}^{3+}$  PL is shown for different perovskite compositions. The perovskite compositions were changed post-synthesis by halide exchange, and their current composition has not been determined, although we could try and estimate it by the excitonic peak position. We see that as the perovskite bandgap energy is reduced slowly, the  $\text{Yb}^{3+}$  emission intensity decreases rather abruptly. While this is roughly in line with Ref. [135], the interpretation could be different in our results, as there are some key differences. The choice of exchange agent in the halide exchange process plays an important role, and in this work we used  $\text{PbBr}_2$ . While the resulting perovskite will have partial to full replacement of the Cl by Br, another unexpected effect is possible; the inclusion of Pb as an exchange agent, is also incorporated into the perovskite. According to literature, the  $\text{Yb}^{3+}$  ions replace the Pb, within the perovskite lattice, so possibly when  $\text{PbBr}_2$  is introduced, the perovskite can self purify and the Yb is replaced by Pb.

To elucidate which of the two mechanisms quenches Yb<sup>3+</sup> emission, we continue to manipulate the perovskite NCs. When the Cl is reintroduced in by use of PbCl<sub>2</sub>, in order to increase the bandgap energy, the Yb<sup>3+</sup> emission does not recover. Therefore we state that in our case Yb is removed, and not just the bandgap change induces Yb<sup>3+</sup> emission quench. This experiment is fundamentally different than the one shown in Ref. [135], as they use a Pb-less halide exchange process, and in that way, only influence the bandgap energy. When exploring a Pb-less halide exchange, using YbBr<sub>3</sub>, the Yb<sup>3+</sup> emission is retained up to the smallest perovskite bandgap that was measured in our work. While the latter finding might be surprising, as Yb<sup>3+</sup> emission is observed with a bandgap smaller than  $2 \times N_{\text{Yb}}$ , we think this results from the sample inhomogeneity. The NC ensemble contains a size distribution, and composition distribution, therefore, those NCs with largest bandgap within the ensemble still have sufficient energy to excite two Yb<sup>3+</sup> ions (marked by the dashed vertical line in Fig. 6.4).

To conclude, the results show that the inclusion of Pb in the halide exchange of Yb<sup>3+</sup> doped CsPbCl<sub>3</sub>, will not only change the perovskite bandgap, but also replace the Yb<sup>3+</sup> by Pb. We observe an immediate decrease in Yb<sup>3+</sup> PL intensity as the bandgap is decreased, indicating that the ejection of Yb<sup>3+</sup> ions is the dominant mechanism in Yb<sup>3+</sup> emission quenching in Pb-contained halide exchange process. This stands in stark contrast to the Pb-free halide exchange process, using YbBr<sub>3</sub>, in which emission is observed for all perovskite bandgaps measured. while the details of the excitation mechanism remain illusive.

## 6.4 Conclusion

This work explored the preparation procedures and PL properties of Yb<sup>3+</sup> ions doped into CsPbCl<sub>3</sub>/Br<sub>3</sub> NCs. Yb<sup>3+</sup>-doped CsPbCl<sub>3</sub>/Br<sub>3</sub> NCs show great promise with extremely efficient sensitization of the Yb<sup>3+</sup> ions. Assisted by quantum cutting, NIR Yb<sup>3+</sup> PLQY of up to 190% have already been reported. [129] Here a maximum Yb<sup>3+</sup> PLQY of 75% was observed, and the excitation of Yb<sup>3+</sup> was found to proceed through the perovskite NCs as the sensitizers.

Furthermore, the possibility of a third Yb<sup>3+</sup> step was explored, in which three Yb<sup>3+</sup> ions are excited per NC, by excess energy provided by high energy excitation. Yet, no evidence was found for this impact-excitation process and it might require a lower bandgap perovskite with different composition.

Lastly, by use of halide exchange of Cl to Br performed on Yb<sup>3+</sup>-doped CsPbCl<sub>3</sub> NCs, the Yb<sup>3+</sup> emission was effectively quenched. This result indicates we can eject the Yb<sup>3+</sup> ions from the perovskites by use of Pb based salts, which then indirectly shows that the optically active Yb<sup>3+</sup> ions take substitutional lattice positions, replacing Pb atoms. Accordingly, Yb<sup>3+</sup>-doping of perovskite NCs should be promoted by Pb-lean synthesis protocols.