

Trends in Lead Degradation of CsPbBr₃ versus CsPbCl₃ Nanocrystals

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Abstract

Perovskite nanocrystals are an emerging field of study due to the low barriers for synthesis, efficient electronic properties, and photoluminescent abilities. The cesium lead halide Cs_nPbX_m shows promising opportunities to improve its stability for usage in electronic and light-harnessing devices such as solar panel cells, but uncertainties about its thermal and chemical stability must be researched in order to create long-lasting, efficient devices. The CsPbCl₃ nanocrystal has been shown to change to Cs₄PbCl₆ after lead depletion in oleylamine solution. This new phase shows higher photocurrents with more defined emission peaks than the I-I-III phase, making the IV-I-VI phase more ideal for use in electronic properties. Through analysis of the CsPbCl₃ nanocrystal spectra in oleylamine solution over time, we find that similar lead degradation in both crystal types cause a blue-shift in emission spectra. Similarities imply possible future interest in chloride crystals as bromide substitutes for photoelectronic usage.

Introduction

With the movement towards alternative sustainable energy, perovskite nanocrystals with the general structure Cs_nPbX_m, (cesium lead halide) have been of interest due to their stability in extreme conditions and their optoelectronic properties. Compared to organic halide perovskite crystals, Cs_nPbX_m have higher melting points and high thermal stability, offering greater prospective for use in solar photovoltaic cells.^[1] Halide perovskite crystals have been demonstrated as effective but chemically unstable semiconductors that can achieve high open-circuit voltages.^[2] Research in both organic-organic and all-inorganic lead halide nanocrystals has found a lack of long-term operational stability be widely-implemented in electronics, especially in the presence of a combination of light, moisture, and oxygen,^[3] but the implementation of the cesium ion has shown significantly greater chemical and thermal stability than organic-organic structures.^[4] Most recently, CsPbBr₃ has been applied in the creation of colloidal quantum dots and solar cells which possess as much as 10.26% efficiency^[5] and maintain this efficiency even in the presence of surface-related defects.^[3]

As a result, perovskite nanocrystals' structures, thermodynamic stability, and optoelectronic properties have been of ever growing interest. In particular, the CsPbBr₃ (I-I-III) structure and its lead depleted derivative Cs₄PbBr₆ (IV-I-VI), induced from ligand addition in polar solvents,^[7,8] have been compared in conductance of photocurrent. Cs₄PbBr₆ exhibited high photocurrents with defined emission peaks, in contrast to the CsPbBr₃ (I-I-III) structure which exhibited less defined photoluminescence emissions.^[7] The amine-induced degradation mechanism has also been observed to yield uniform Cs₄PbBr₆ sheets and nanoplatelets, suggesting an extended degree of tunability of the desired Cs₄PbBr₆ structure.^[7,8] One possible alternative to bromine in the CsPbBr₃ structure may be chlorine. Although CsPbCl₃ has shown lower photoluminescent quantum yield in the blue visible range^[9,10], the transformation of CsPbCl₃ into a lead degraded phase may provide greater insight on similarities with CsPbBr₃ phase transformation and potential new characteristics of a lead depleted CsPbCl₃ structure. This study aims to determine if similar conditions will cause degradation in the CsPbCl₃.

Methods

8nm-edge length cubic CsPbBr_3 and CsPbCl_3 nanocrystals were synthesized under established standard procedures and dissolved in dodecane within a well plate. Varying amounts of oleylamine (OLA) were added as additives in a 1mm well. The absorbance and emission spectra of the nanocrystal solutions were measured over various hour by hour intervals at room temperature and ambient conditions. Data analysis was performed through Python Jupyter Notebook.

Results and Discussion

The addition of oleylamine has resulted in the formation of the lead-depleted phase in some of the CsPbBr_3 nanocrystals with the characteristic peak at $\lambda=310\text{nm}$ (Fig. 1). This peak is indicative of the transformation from the initial 1-1-3 phase to the 4-1-6 lead-depleted phase.^[6] This transformation is primarily due to the high affinity between the nucleophilic $-\text{NH}_2$ functional group in OLA and the Pb cations in the perovskite structure to form a Pb-OLA complex.^[5]

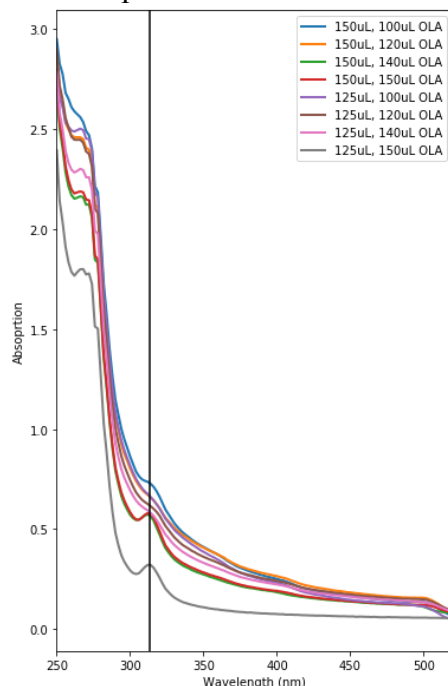


Figure 1. Absorption profile of Cs_4PbBr_6 nanocrystals

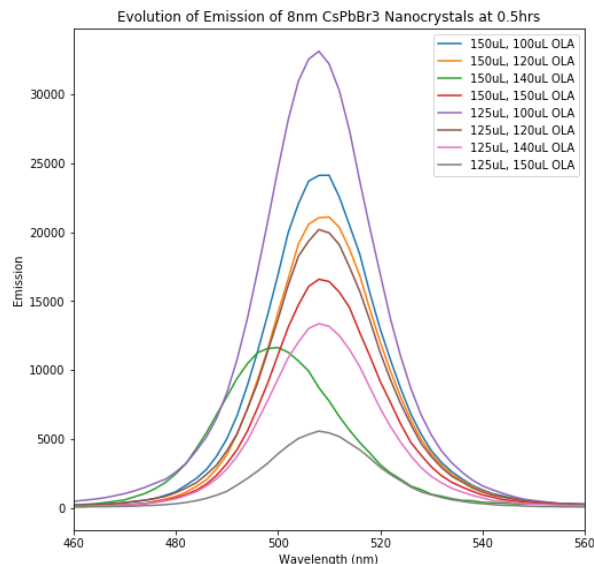


Figure 2. Emission Profile of CsPbBr₃ nanocrystals with varying OLA amounts at 0.5hr

The Cs₄PbBr₆ nanocrystals emit green light at ~508nm, (Fig. 2) which is consistent with the emission of bulk and nanocrystal Cs₄PbBr₆.^[5,11] This confirms that the introduction of OLA induces the degradation of the CsPbBr₃ nanocrystals. The emission of Cs₄PbBr₆ was documented to observe the stability of the synthesized Cs₄PbBr₆ (Fig 3).

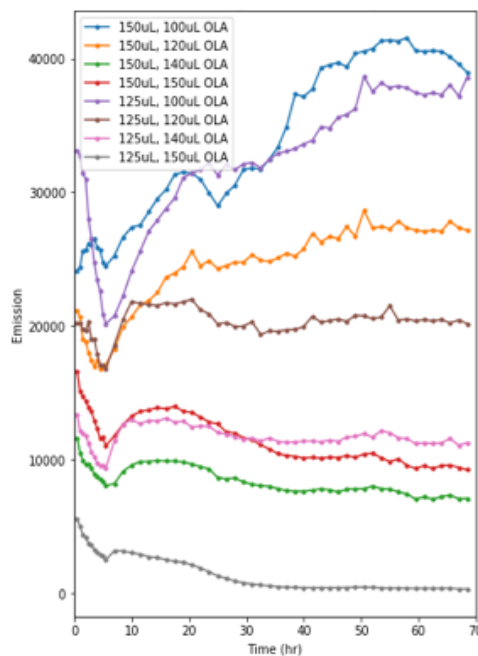


Figure 3. Evolution of Emission of Cs₄PbBr₆ nanocrystals at λ_{\max}

It is of note that while the general trend indicates a decrease in the emission over time, a smaller Pb/OLA ratio results in an increasing emission over time. Although the mechanism as to why

this happens is unclear, we hypothesize that this might indicate the transformation of more CsPbBr_3 nanocrystals into Cs_4PbBr_6 .

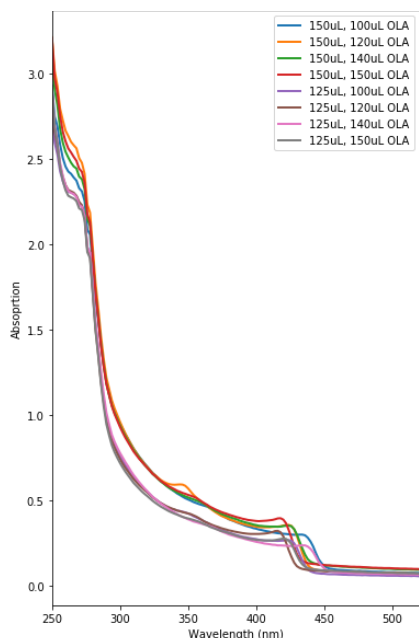


Fig. 4 Absorption of 8nm CsPbCl_3 nanocrystals at 50.5 hrs

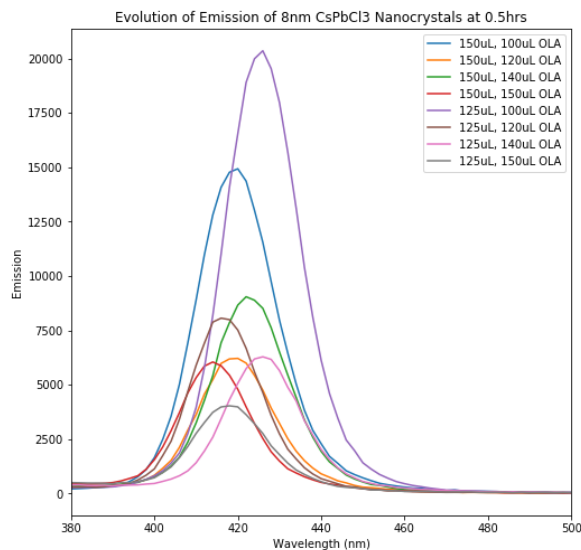


Fig. 5 Emission profile of 8nm CsPbCl_3 nanocrystals

Fig. 4 and Fig. 5 illustrate the absorption and emission profiles (respectively) of 8nm CsPbCl_3 nanocrystals with various amounts of oleylamine. Compared to the emission of the CsPbBr_3 nanocrystals, the CsPbCl_3 has a more dispersed distribution of λ_{max} . Figure 6 shows the emission at the wavelength of maximum emission for each of the CsPbCl_3 trials. It is observed that emission generally increases steadily for the CsPbCl_3 nanocrystals. This may point to an increased stability in the emission of CsPbCl_3 over CsPbBr_3 , which was observed to degrade over time. The synthesis of Cs_4PbBr_6 but not Cs_4PbCl_6 was observed in the experiment. Cs_4PbCl_6 emits light at $\sim 520\text{nm}$, whereas the CsPbCl_3 samples synthesized in this experiment have emission centered at $\sim 420\text{nm}$. This may be due to an incompatibility in the ligand used for the ligand-assisted transformation of the perovskite nanocrystal, or the closer spacing between Pb and Cl vs. Pb and Br in the perovskite crystal structure.

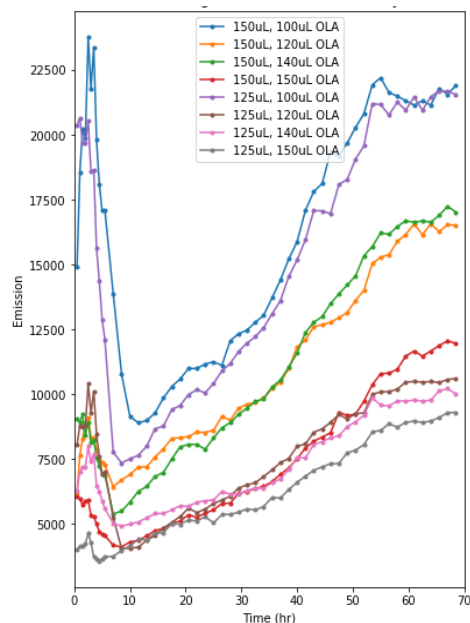


Figure 6. Emission over time at λ_{max} of 8nm CsPbCl₃ nanocrystals

Conclusion

The amine-induced degradation of the synthesized cubic CsPbBr₃ nanocrystals to a lead-depleted phase (presumably IV-I-VI, IV-II-VI, or IV-III-VI) is observed by the presence of the characteristic absorption peak at 313nm. A time series analysis of the emission of the CsPbBr₃ nanocrystals indicate a general decrease in the emission at greater oleylamine (OLA) to lead (Pb) ratios, although an increasing trend in the emission is shown at lower OLA/Pb ratios. The decrease in emission at higher OLA/Pb ratios is indicative of the morphological transformation of the cubic CsPbBr₃ to polygonal Cs₄Pb_xBr_y. The emission spectra also demonstrated a shift in the wavelength of maximum emission from 508nm to 506nm for the CsPbBr₃ nanocrystals, indicating a decrease in the size of the nanocrystal.

Both the CsPbBr₃ and CsPbCl₃ nanocrystals exhibit a decrease in emission upon the onset of addition of OLA, followed by a subsequent increase in emission. It was observed that the addition of OLA results in a more disperse size distribution in the CsPbCl₃ nanocrystals, as observed in the emission and absorption profiles, compared to the CsPbBr₃ nanocrystals. The lead depletion evident in CsPbBr₃ nanocrystals may be due to the difference in size of the edge length of the crystal lattice as well as the holes in the crystal structure. The larger size of the Br⁻ ion allows for the Pb²⁺ cation to be more easily removed from the crystal lattice, resulting in a lead depleted phase in CsPbBr₃ but not in CsPbCl₃. The researchers recommend the use of XRD (X-Ray Dispersion) to accurately determine the molar composition of each element (Cs, Pb, and X=I, Cl, Br, F) to ascertain the identity of the lead-depleted product. Further research to understand characteristics of this lead-depleted product may also show further insight into the potential benefits or loss when transitioning from the original I-I-III structure into the lead-depleted structure.

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