Stability of Sn based inorganic perovskite quantum dots

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Abstract

Metal halide perovskite crystal structures have emerged as a class of optoelectronic materials, which combine the ease of solution processability with excellent optical absorption and emission qualities. However, the most promising perovskite structures rely on lead as a cationic species, thereby hindering commercial application. The replacement of lead with non-toxic alternatives such as tin has been studied in bulk but not in nanocrystals. In this work, we synthesize Sn and Pb based alloy perovskite nanocrystals by direct synthesis method, taking mixture of Pb and Sn precursors in the desired ratio leading to quantum dots (QDs) of CsPb₁⁻ₓSnₓBr₁₋₃, with successful Sn incorporation into the host lattice. As colloidal stability of these QDs is a crucial factor for device applications, we have studied the stability of the QDs under different conditions for these Sn based QDs and have found them to degrade faster upon using anti-solvents during washing process. In order to stabilize them, we have devised a purification method that is also discussed. Further, even though the optical and crystal structure stability in some of the inorganic perovskites leaves much room for improvement, so far there have been no studies on the structure property correlation. Here we study their structural purity and their optical stability after understanding the structure property correlation in CsPbI₃ and CsPbBr₃ perovskite structures. The stability of Sn doped perovskites obtained from a logical understanding of structure property correlation is found to be extremely stable across the series of compounds for up to three months.

1. Introduction

Intense development of organometallic and inorganic lead halide systems have led to a dramatic surge in the efficiency of the opto-electronic applications including photovoltaics [1, 2], light emitting diodes (LEDs) [3] and lasers [4]. This is largely powered by sustained research interest to produce cost-competitive, facile, and environmentally friendly technologies. Among these, the perovskite systems exhibit numerous advantages like abundance of materials, flexibility, and simple processing leading to low production cost which directly contributes to the competitiveness with other commercial technologies like indium tin oxide. Despite the impressive progress in lead-halide perovskites, several challenges related to stability upon prolonged exposure to light, humidity, and high temperature as well as the development of suitable large-scale manufacturing processes are yet to be addressed. In this context, the most unsettling flaw of these perovskite materials, that is also a stumbling block for the large scale applications, is the toxicity of the dissolvable lead leading to environmental concerns. This has led to a great deal of interest in replacing Pb with less toxic metals such as Bi [5], Sn [6], Ge [7] but the efforts have largely been unsuccessful due to the highly unstable nature of these compounds under ambient conditions. In this context, aiming for the retention of optoelectronic properties, tin based perovskites have attracted most attention due to its similar ionic radii (Pb: 1.19 Å to Sn: 1.18 Å) within the same group of the periodic table. A quick inspection of fundamental physical properties of tin based perovskites lead to remarkable similarities with their lead based counterparts. Therefore, Pb substitution by Sn should cause no obvious lattice
distortion in perovskites [8]. Cesium tin iodide (CsSnI₃) has direct bandgap of around 1.3 eV [9], which is even narrower and more attractive for NIR applications than those of their Pb-based analogs. After exposure to ambient air, the Sn-based perovskites degrade to Sn⁺⁺ becoming SnO₂, which is an environment-friendly material. Though, recently Pb free CsSnX₃ QDs have been reported to exhibit visible to NIR bandgap tunability (2.8–1.8 eV), they have failed to perform in the field of optoelectronic devices due to very low PL QY and poor stability [10].

Hence though in principle we expect to reproduce similar efficiencies of these materials, the tin based perovskites are known to be extremely unstable. While a lot of research has gone into exploring how to stabilize and improve the efficiency of tin based perovskites, the fundamental reason for this instability has not been explored. In this work we explore means of stabilizing the Sn doped cesium lead halide systems along with maintaining the structural phases to study the effect of crystal structure on its optical properties. Since structure-property correlation is largely unexplored even in the lead based perovskits, we have first studied the same in a wide range of lead based perovskites ranging from highly stable and luminescent materials like CsPbBr₃ to the unstable CsPbI₃. We then dope tin in lead based perovskites to understand if similar structural features lead to decay of its optical properties.

2. Experimental methods

Although optical properties of colloidal perovskite QDs can easily be tailored through halide exchange reactions [11, 12], cation exchange to obtain mixture of Pb and other metals have been rarely attempted. Recently, replacing a small percentage of Pb with divalent atoms such as Mn⁺⁺, has been tried by taking mixture of Pb and Mn precursors to achieve characteristic Mn dopant emission [13]. Post synthetic cation exchange on CsPbBr₃ by Sn, Cd, Zn to replace Pb has also been reported recently [14]. However, direct synthesis of perovskite QDs based on Sn/Pb mixture has not been reported so far. Here, in this work, we take mixture of Pb and Sn precursors in the desired ratio to replace Pb with Sn leading to QDs of CsPb₁₋ₓSnₓ(Br/I)₁ₓ with successful Sn incorporation into the host lattice.

Perovskite NCs were prepared according to the method described by Protesescu et al [15]. Stoichiometric mixtures of PbI₂ and PbBr₂ were used for the synthesis of undoped NCs, whereas stoichiometric mixtures of PbI₂ and PbBr₂ with SnI₂ and SnBr₂ were taken for the synthesis of Sn doped CsPb(Br/I)₁ₓ perovskite NCs. Detailed synthesis methods and the details of characterization are described in supporting information.

The QDs were first washed by adding equal volume of tert-butanol and centrifuging at speed of 5000 rpm for 5 min. The supernatant was discarded and the particles were re-dispersed in hexane. However, QDs obtained by this method was later found to be colloidaly unstable. For obtaining colloidaly stable QDs, the crude solution was cooled down by water bath and QDs were separated by centrifuging for 10 min at 5000 rpm. The precipitated QDs were dispersed in hexane and this suspension was centrifuged again for 5 min at 10 000 rpm, after which the precipitate, containing unreacted precursors, larger QDs and agglomerates, was discarded. The supernatant containing the QDs was then stored under refrigeration.

3. Results and discussion

Structure property correlation in lead halide perovskites are first studied to understand the source of instability of optical properties. It has been well known in literature [16] that among the halides, iodides are known to be optical unstable when exposed to air and moisture. Hence, we first characterized the CsPbI₃ QDs as shown in figure 1. Figure 1 (a) shows the absorbance and PL of CsPbI₃ measured immediately after synthesis (red plots) and measured after 10 days. It is clearly evident that not only the PL intensity died down within this period but the absorption was heavily blue-shifted similar to available literature [16] showing clear transformation from optically active to inactive phase. This could possibly be due to a phase transition during this period as CsPbI₃ QDs are known to be stabilized in both cubic and orthorhombic phases. This was further verified by XRD patterns of these two samples taken over a period of 10 days that is shown in figure 1 (b), which shows structurally unstable CsPbI₃ transforming from cubic to orthorhombic phase under ambient conditions matching the available literature [16]. Hence even though stabilising the cubic phase is a challenging task, the difference in structural information between both the crystal phases and PL features can be a useful tool to study effect of Sn doping taking CsPbI₃ as starting host QDs. The PL emission peak at 695 nm for cubic CsPbI₃ which is dark brown in colour transforms to the yellow orthorhombic phase that is PL inactive under continuous exposure to air, atmosphere and moisture.

However, in contrast to CsPbI₃, wherein direct evidence about stable phase could be obtained from XRD and optical absorption data, from the perspective of structure property correlation, the XRD pattern and the band gap of CsPbBr₃ does not prove to be very useful. The band gap of CsPbBr₃ is not different for both cubic and
orthorhombic phases unlike CsPbI$_3$. Additionally, it is nearly impossible to differentiate between the cubic and orthorhombic phases between QDs of CsPbBr$_3$ due to similarities in the XRD patterns of the bulk. Hence direct correlation between structural stability and PL emission cannot be studied.

Upon establishing this correlation, we now turn our attention to the Sn doping in these perovskite systems. Due to the speed of decomposition and the instability of cesium lead iodides, doping Sn in CsPbI$_3$ to study the structure property correlation is non-trivial, even though CsSnI$_3$ is of higher relevance in applications. In order to overcome this shortcoming, we started doping Sn in CsPbBr$_3$ as it is well known in literature that CsPbBr$_3$ is more stable than the CsPbI$_3$ allowing a better chance to correlate the properties with the structural information.

Sn doped CsPbBr$_3$ for varying Sn concentrations were characterized by XRD as shown in figure 2(a). From the figure, it is evident that the Sn-doped CsPbBr$_3$ shows same characteristic diffraction peaks as undoped CsPbBr$_3$. However, due to a large structural similarities between Sn and Pb based compounds as well as broad features arising due to the nanocrystal size, though a shift in the peak positions can be observed due to Vegard’s law, it is not possible to confirm the presence or absence of phase segregation due to Sn doping from XRD patterns.

Figure 2(b) shows the optical absorption and PL data upon Sn incorporation which shows blueshift in both the absorbance and steady state photoluminescence spectra. Undoped CsPbBr$_3$ has a band gap of 509 nm (2.44 eV) which upon Sn doping upto 10%, blueshifts systematically up to 496 nm (2.5 eV). This is not surprising as partial replacement of Pb$^{2+}$ by several isovalent ions like Sn$^{2+}$, Cd$^{2+}$, and Zn$^{2+}$ is known to give rise to blueshift in the optical spectra which is attributed to the lattice contractions [14]. Further increase in Sn percentage leads to severe shift in the band gap, possibly due to phase segregation or due to the breakdown on the perovskite
structure. In addition, it is evident that attempt to increase the Sn dopant in the host system leads to optically unstable QDs. However, similar to CsPbBr₃ compounds, direct correlation of structure with optical properties seem impossible.

In order to overcome both these shortcomings, we studied stability of mixed halide systems as a function of Sn doping with special emphasis on sample purification. In order to achieve this, we used SnBr₂ as a cation precursor source in the synthesis such that in addition to Sn incorporation, anionic mixing between Br and I can improve the structural stability and optical stability.

Stoichiometric mixtures of SnBr₂ and PbI₂ was used for synthesis of Sn-doped CsPb(Br/I)₃ QDs. Normal purification techniques involve mixing the “as prepared” samples with equal quantity of tert-butanol and centrifuging at 5000 rpm for 10 min. However, these antisolvents like tert-butanol not only precipitate the QDs and the excess unreacted precursors [15] but also facilitate removal of the surface ligands which can lead to exposure of QDs to air and moisture, thus enhancing the rate of degradation. Presence of unreacted precursors are favourable for well known ion migrations giving rise to phase segregated perovskite QDs reported earlier [17]. Hence it is important to introduce an effective way of purifying as synthesized QDs which can be both structurally and optically stable.

Typical XRD patterns of Sn doped CsPb(Br/I)₃ QDs for various Sn dopant percentages are shown in figure 3(a). The sizes as obtained from the broadening of the XRD peaks is estimated to be about 11.5 ± 1 nm from the Scherrer formula. Representative TEM and HRTEM images for 2.1% Sn doped CsPb(Br/I)₃ QDs are shown in figure S1 is available online at stacks.iop.org/MRX/6/114004/mmedia in the supporting information with QDs showing average size of 11.7 ± 1.5 nm, in accordance with the sizes obtained from XRD patterns.

![XRD and Absorption spectra](image-url)
From the figure 3 (a) it is evident that upon Sn incorporation it is seen that orthorhombic peaks started arising which, in turn, led to less intense PL emission compared to their cubic counterparts. Further presence of small mixture of orthorhombic phase led to faster degradation and ion migrations of the QDs at ambient conditions. Hence we developed a modified purification strategy of the Sn-doped QDs for the conservation of the structural integrity. The as synthesized QDs were centrifuged at high speed for around 10 min to precipitate the QDs and the supernatant containing solvents like ODE was discarded. The precipitate contained both Sn doped perovskite QDs and excess ligands and precursor complexes. To remove all the unnecessary components that are known to hinder the QDs performance were removed by dissolving the precipitate in hexane and centrifuging at high speed (10 000 rpm) for 3 min. By doing this, unreacted precursors precipitated out of hexane. Further the supernatant was collected and the process was repeated multiple times to remove the unreacted precursors. The schematic of the purification process is shown in figure 3 (b). These samples are referred as purified samples in the rest of the manuscript.

The purified samples were preserved in refrigerator for longer stability. XRD patterns of Sn-doped QDs purified by above method is shown in figure 3 (c) which show that all the samples retain cubic crystal structure and do not contain any of the impurity peaks. Hence by selective and careful precipitation of the QDs after the reaction, cubic Sn doped CsPb(Br/I)3 QDs can be synthesized.

Optical stability of the QDs were studied over a period of 10 days kept under ambient conditions and were compared with QDs washed using tert-butanol. The results are summarized in figure 4. Figure 4(a) shows the PL spectra for 2.1% Sn doped sample washed using tert-butanol. Over a period of 10 days we see that the PL blueshifts in addition to reduced PL intensity. The facile phase segregation in this group of systems are well known in literature [18–21] and reduced ligands can further hasten this process. Hence this blueshift in the spectra could possibly arise due to phase segregation of the QDs and phase transition of the iodine rich phase into the optically inactive orthorhombic phase. Due to this phase segregation, the ratio of optically active phase contains an increased Br/I ratio resulting in the blueshift of the spectra in addition to deterioration of the PL intensity. In contrast to this highly unstable QDs, purification using repeated centrifugations leads to more stable QDs with no shift in PL emission spectra and minimal intensity fluctuations giving an emission peaked at 588 nm as shown in figure 4(b). Figure 4(c) shows variation in PL emission wavelength and intensity plotted over a period of 10 days for the samples washed using tert-butanol as well as the purified samples. As observed from the spectra, samples washed with tert-butanol showed a continuous blueshift while the purified samples showed very high colloidal stability and the PL emission wavelength was invariant for over 10 days. Similarly PL intensity...
variation showed uniform emission intensity for purified QDs while the samples washed by tert-butanol demonstrated a dramatic variation in its intensity as also shown in figure 4(c). Similar colloidal stability studies were also carried out for 4.3% Sn-doped perovskite QDs. The PL emission spectra for washed and purified QDs over a period of 5–7 days are respectively shown in figures S2(a) and S2(b). The conclusions are similar suggesting that the proposed purification method indeed helps the QDs to retain better colloidal stability. Figures S2(c) and S2(d) show variation of PL emission and its intensity over a period of 10 days demonstrating very high colloidal stability for Sn doped perovskite QDs.

However, having good colloidal stability and optical emission quality over a period of 10 days are not sufficient for device application perspective. Hence it is important to know the structural stability of these QDs over long term. As we have seen that PL emission is directly correlated to structural properties, even presence of minor surface degradation and exposure can lead to huge changes in emission quality and PL quantum yield.
Additionally, for device applications, these QDs have to be spin coated to a film and once they are cast on a film, the chances of reduction in PL QY and transformation from cubic to orthorhombic phase transition are much higher.

To understand the long term stability of the Sn doped QDs, we performed XRD and PL spectra after 3 months and the results are shown in figures 5(a) and (b) respectively. The films exposed to air, moisture and ambient light kept at room temperature showed signatures of slight degradation and showed presence of slow but definite phase transition. Prolonged exposure to ambient light and moisture and atmosphere is shown to degrade the structural features and PL QY and it has been shown that the encapsulation of these QDs within polymer matrices enhances the stability [22]. The stability of these QDs is also enhanced by the use of various methods like embedding the QDs in silica microsphere [23, 24] or in PMMA polymer matrix [15, 25]. Interestingly, we observed ultra high structural stability for these QDs preserved in glovebox as seen from figure 5(a). Hence it is recommended to preserve the QDs, especially films under inert atmospheres for long term stability. Figure 5(b) shows normalised PL spectra for all the Sn doped CsPb(Br/I)3 taken after 3 months showing no blueshift and maintaining narrow emission linewidth with high PL QY.

In summary, direct synthesis of Sn doped CsPb(Br/I)3 by hot injection method is demonstrated and fast degradation of cubic phase to orthorhombic phase is systematically studied by directly correlating the structural information with PL emission characteristics. Presence of unreacted precursors and removal of surface ligands are found to be accelerators of structural transformation and modified purification of as synthesized QDs were employed to obtain colloidal stability. Long term stability of these QDs over a period of 3 months were studied and it is found that continuous exposure to ambient air, moisture and light can lead to partial degradation and it is preferred to store the films of QDs in inert atmosphere. Colloidal stability study of these QDs under different conditions reveal their stability under ambient conditions which is apt for various device applications such as LEDs, photo detectors and lasers. By incorporating Sn into the lattice of Pb based perovskite QDs, these new class of materials may prove beneficial for a number of applications.
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