White light emission from lead-free mixed-cation doped Cs₂SnCl₆ nanocrystals†

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We have designed a synthesis procedure to obtain Cs₂SnCl₆ nanocrystals (NCs) doped with metal ion(s) to emit visible light. Cs₂SnCl₆ NCs doped with Bi³⁺, Te⁴⁺ and Sb³⁺ ions emitted blue, yellow and red light, respectively. In addition, NCs simultaneously doped with Bi³⁺ and Te⁴⁺ ions were synthesized in a single run. Combination of both dopant ions together gives rise to the white emission. The photoluminescence quantum yields of the blue, yellow and white emissions are up to 26.5, 28, and 16.6%, respectively under excitation at 350, 390, and 370 nm. Pure white-light emission with CIE chromaticity coordinates of (0.32, 0.33) and (0.32, 0.32) at 340 and 370 nm excitation wavelengths, respectively, was obtained. The as-prepared NCs were found to demonstrate a long-time stability, resistance to humidity, and an ability to be well-dispersed in polar solvents without property degradation due to their hydrophilicity, which could be of significant interest for wide application purposes.

1. Introduction

Metal halide perovskites (MHPs) and their analogues have recently emerged as new optoelectronic materials with outstanding characteristics for efficient solid state lighting applications.1–4 MHPs have been successfully used to fabricate white-light emitting diodes (WLEDs).5–8 There are two possibilities to provide a white-light emission from the MHP emitters: (i) use of a mixture of emitters of different colours, and (ii) use of one-type emitters with a broad photoluminescence (PL) spectrum. The former approach, which has been mostly studied for lead halide perovskites,9 is possible for the band-to-band emitting MHP semiconductors. However, a formation of blends of solution processed nanocrystals (NCs) is limited because of the anion exchange processes and hence the formation of mixed halide NCs with a new emission.10–13 Typically, to avoid the anion exchange and provide a white emission in a mixture of different light-emitting perovskite NCs, wrapping the perovskite NCs by silica or coating by a polymer or PbSO₄-oleate is used,14–17 or mixing a MHP with another emitter of different nature that complements its emission in order to obtain a white color, for example as in case of combining with carbon quantum dots.18 A white emission from single MHP emitters is usually provided by broadband PL from self-trapped excitons (STE), where the categorized materials are mostly 1D or 2D metal halide hybrid organic–inorganic layered perovskites,19–23 or all-inorganic lead-free MHPs.24–26 The white emission from single MHPs has been successfully achieved for polycrystalline thin films or NCs. Needless to say, lead-free MHPs have been studied from this point of view more intensively than their Pb-based counterparts because of their low toxicity. Among these MHPs, double halide perovskites (DHP) are a class of materials with predominantly reported STE characteristics to provide the white-light emission.27

The general formula of DHP is A₂B[I]B′(III)X₆, where B[I]X₆ and B′(III)X₆ are metal–halide octahedra alternatively corner-shared to each other with a 3D connected geometry. When one of the B-site is omitted from the crystal lattice by placing a virtually-vacant octahedra, which is apparently connected to each of the [BX₆] entity, such kind of DHP is known as vacancy-ordered DHP, formulated as A₂BX₆.27,28 Noteworthy, the oxidation state of the B-site becomes “+4”. Examples of vacancy-ordered DHPs are: Cs₂SnX₆, Cs₂TeX₆, Cs₂ZrX₆, Cs₂PdX₆ etc. [X = Cl, Br, I], which have been experimentally reported so far according to their synthesis and optoelectronic properties. A high oxidation state of the B-site cation (+4) is beneficial for a...
stability of these materials under ambient conditions.\textsuperscript{29–34} Since the metal halide octahedra are not corner-shared to each other, these are from the family of 0D materials. Recently, Cs\textsubscript{2}SnCl\textsubscript{6}, a class of 0D vacancy-ordered DHP, has been reported with dopant-induced STE emission with Bi\textsuperscript{3+}, Te\textsuperscript{4+} and Sb\textsuperscript{3+} as dopants emitting blue, yellow and red photoluminescence (PL), respectively, with high PL quantum yields (PLQYs).\textsuperscript{35–39} Doping with Bi\textsuperscript{3+} and Sb\textsuperscript{3+} has been also extensively studied for 3D DHPs to provide broadband emission for optoelectronic applications.\textsuperscript{40–46} In a recent work Zhou et al. reported white-light emission from a mixture of Bi\textsuperscript{3+} and Sb\textsuperscript{3+} co-doped Cs\textsubscript{2}NaInCl\textsubscript{6} DHP.\textsuperscript{47} Apart from the role as dopants, Bi\textsuperscript{3+}, Sb\textsuperscript{3+} and Te\textsuperscript{4+} have also been successfully used as ideal B-site cations in order to provide alternative lead-free perovskite semiconductors for optoelectronic applications.\textsuperscript{30,48,49}

So far, 0D perovskites possessing STE emission characteristics based on their transient lattice deformation upon photo-excitation have been reported.\textsuperscript{46,51} While undoped Cs\textsubscript{2}SnCl\textsubscript{6} does not possess any PL, an incorporation of a small percentage of one of the aforementioned dopants results in visible PL with high PLQY.\textsuperscript{35,38} Several reports on their PL and down conversion electroluminescence have been published.\textsuperscript{35,36} However, to the best of our knowledge, doped Cs\textsubscript{2}SnCl\textsubscript{6} has been synthesized in the form of powder, while ligand capped colloidal NCs have been studied only for Sb\textsuperscript{3+}-doped Cs\textsubscript{2}SnCl\textsubscript{6} among these.\textsuperscript{52} Powder materials are inconvenient for subsequent deposition in thin films, as optoelectronic applications mostly require. In this sense, the material synthesis in the form of NCs has an enormous advantage of allowing easy deposition of NCs forming thin films.\textsuperscript{18,53} Alongside, these NCs demonstrated lower PLQY in comparison to their bulk phosphors, having a similar trend comparing with previously reported works.\textsuperscript{46,52} Herein, we report the colloidal synthesis of Cs\textsubscript{2}SnCl\textsubscript{6} NCs with a broad range of doping elements such as Bi\textsuperscript{3+}, Sb\textsuperscript{3+} and Te\textsuperscript{4+}, using a cost-effective synthesis methodology. We have chosen NCs with Bi\textsuperscript{3+} and Te\textsuperscript{4+} as dopant ions, which provide blue and yellow emission, respectively. We have also successfully synthesized white-light emitting dual-doped Cs\textsubscript{2}SnCl\textsubscript{6} NCs in a one synthesis containing both of the Bi and Te dopants up to 0.8 and 2.8\%, for 30 and 50\% of initial loading of the Bi and Te-precursors with respect to Sn-precursors, which provide a combination of blue and yellow emissions from the individual dopant ions without any intervention of other impurity phases. Providing white light emission by mixing individual entities emitting light of different colors is difficult for lead halide perovskites, as has been reported\textsuperscript{9} and previously commented because of the anion exchange processes between NCs of different types. In our synthesizing method, both cation dopants are incorporated together, and hence we obtain the white light emission by \textit{in situ} synthesis. We propose a proficient light-emission application of these NCs because of their abundance and easy-to-prepare using a cost-effective methodology. Besides, these NCs demonstrated a stability on harvesting into polar solvents due to their hydrophilicity, which could be beneficial for wide application purposes.

2. Experimental section

2.1 Chemicals

Cesium acetate (99.9%, Sigma Aldrich), tin(II) acetate (Sigma Aldrich), bismuth(III) acetate (99.99%, Sigma Aldrich), tellurium(IV) oxide (99%, Sigma Aldrich), antimony(III) acetate (99.9%, Sigma Aldrich), oleic acid (90%, Sigma Aldrich), 1-octadecene (ODE; Sigma Aldrich), hydrochloric acid (HCl; ACS reagent, 37%, Sigma Aldrich), acetone, isopropanol, N-methyl-2-pyrrolidone.

2.2 Synthesis

2.2.1 Bismuth and antimony doped Cs\textsubscript{2}SnCl\textsubscript{6} nanocrystals.

In a three-necked flask, 46 mg of tin(II) acetate (0.2 mmol), 76 mg of cesium acetate (0.4 mmol), and different amounts of bismuth(III) acetate (10–50\% wrt tin acetate) were loaded together along with 1 ml of oleic acid and 10 ml of ODE, and degassed under vacuum at 120 °C for 1 hour. A clear solution was obtained which confirms the formation of metal oleates, and the solution was filled with nitrogen. This whole procedure was carried out in inert condition in order to prevent the unwanted reaction under air atmosphere. The next step of the reaction was the halogenation of the metal precursor solution. The metal precursor solution was cooled down to room temperature and the solution transferred to a beaker containing 1 ml of HCl. The beaker containing HCl (in aqueous medium) and metal oleates (in organic medium) were sonicated for 10 minutes. The solution turned yellow after the addition of HCl. After that, 10 ml of acetone was added to the beaker, and stirred at room temperature for 30 minutes. Upon the addition of acetone to the solution, the solution turned white, which confirms the formation of nanocrystals. The precipitate was collected by centrifugation at 5000 rpm for 5 minutes, and washed with acetone for two times at the same centrifugation rate to remove the excess of water from HCl. Finally, the nanocrystals were dispersed in toluene or acetone.

For the preparation of antimony doped Cs\textsubscript{2}SnCl\textsubscript{6} nanocrystals, the same procedure was followed. Antimony(III) acetate was taken instead of bismuth(III) acetate. The solution turned white after the HCl treatment and remained with the same white color upon the addition of acetone. The purification procedure was the same as for bismuth doped nanocrystals.

2.2.2 Tellurium(IV) doped Cs\textsubscript{2}SnCl\textsubscript{6} nanocrystals. In a three-necked flask, 46 mg of tin(II) acetate (0.2 mmol) and 76 mg of cesium acetate (0.4 mmol) were loaded together along with 1 ml of oleic acid and 10 ml of ODE, and degassed under vacuum at 120 °C for 1 hour. Once a clear solution of metal precursors was observed, the reaction flask was filled with nitrogen and cooled down to room temperature. In a beaker, TeO\textsubscript{2} (10–50\% wrt tin acetate) was dissolved in 1 ml of HCl, and the metal precursor solution was added onto it. The solution was sonicated for 10 minutes followed by the addition of acetone, and stirred for 1 hour under ambient condition. The temperature of the reaction medium was maintained at 40–50 °C. The solution turned black just after the addition of acetone, and slowly changed the color to pale yellow over an
transmittance spectra were obtained by a conversion of absor-
acetone were drop casted on top of a quartz substrate. The
using an integrated sphere unit. The samples dispersed in
collected from PerkinElmer UV-Vis-NIR spectrophotometer
were performed using a D8 Advance, Bruker-AXS X-ray di-
2.3 Characterizations
UV-Vis absorbance. UV-Vis absorption spectra were
from the individual dopant centers, analogous white
emission of both Bi$^{3+}$ and Te$^{4+}$ dopants provided a white-light emission as a result of combination of the blue and yellow emissions from the individual dopant centers, analogous white emission was also observed when individual Bi$^{3+}$ and Te$^{4+}$ doped NCs were mixed post-synthetically (Fig. S1a†). Our attempt of in situ preparation of Sb$^{3+}$, Bi$^{3+}$ and Te$^{4+}$ triple-
doped Cs$_2$SnCl$_6$ NCs failed, giving rise only to a very poor red emission. However, a post-synthetic mixing of different blue, yellow (or white) and red emissive NCs produced a warm white-light emission (Fig. S1b†). The synthesized NCs allows easy preparation of NC thin films, see Fig. 1c and d. Crystal structures of undoped Cs$_2$SnCl$_6$ and the B-site doped Cs$_2$SnCl$_6$ is provided in Fig. 1e, where the tin halide octahedra (SnCl$_6$) are not connected to other octahedra, or virtual vacant corner-shared octahedra are connected to each other. The metal-ligand coordination is octahedral for the dopant metal chlor-

3. Results and discussion

Metal ion(s) doped Cs$_2$SnCl$_6$ NCs were synthesized by using a ligand-assisted wet chemical method. Oleic acid was used as a ligand, and 1-octadecene (ODE) as solvent. The synthesis procedure is a two-step process. For preparation of Bi$^{3+}$-doped (or Sb$^{3+}$-doped) Cs$_2$SnCl$_6$ NCs, the first step was the formation of metal oleates, by reacting Cs-acetate, Sn(II)-acetate, and Bi(II)-acetate (or Sb(II)-acetate) with oleic acid. In the second step, hydrochloric acid (HCl) was introduced to the metal–oleate solution, and the halogenation reaction took place at the interface of an organic–aqueous layer. For preparation of Te$^{4+}$-doped Cs$_2$SnCl$_6$, we used TeO$_2$ as dopant precursor, which was added to HCl for complete dissolution followed by the second step of reaction. Noteworthy, we incorporate TeO$_2$ into HCl instead of adding it simultaneously with the metal precursors, because TeO$_2$ would remain unreacted with oleic acid in the first step of reaction. The quantity of dopant precursor was varied from 10% to 50% in order to obtain the best photoluminescence for Bi and Te-dopants with respect to Sn-precursor. Dual-doped (Bi$^{3+}$/Te$^{4+}$) Cs$_2$SnCl$_6$ NCs were synthesized by the combination of Bi-doping and Te-doping strategies. Details of the reaction scheme are provided in Fig. 1a. The synthesis methodology is established as a generic method to prepare individual Bi$^{3+}$, Te$^{4+}$, and Sb$^{3+}$ doped or dual-doped (Bi$^{3+}$/Te$^{4+}$) Cs$_2$SnCl$_6$ NCs. The as-prepared NCs were finally dispersed in acetone or toluene. Besides, the NCs were well dispersed in N-methylpyrrolidone (NMP) and isopropanol without any deterioration of optical properties and/or quick precipitation. Detailed synthesis method is provided in the Experimental section. A digital image of the blue, yellow, red and white photoemission of Bi$^{3+}$, Te$^{4+}$, and Sb$^{3+}$, and dual (both the Bi$^{3+}$ and Te$^{4+}$) doped Cs$_2$SnCl$_6$ nanocrystals under 365 nm UV lamp is provided in Fig. 1b. The PLQYs of the corresponding emissions were 26.5, 28, <1, and 16.6% under the excitation at 350, 390, 350, and 370 nm, respectively. While an in situ introduction of both Bi$^{3+}$ and Te$^{4+}$ dopants provided a white-light emission instead of adding it simultaneously with the metal precursors, because TeO$_2$ would remain unreacted with oleic acid in the first step of reaction. The quantity of dopant precursor was varied from 10% to 50% in order to obtain the best photoluminescence for Bi and Te-dopants with respect to Sn-precursor. Dual-doped (Bi$^{3+}$/Te$^{4+}$) Cs$_2$SnCl$_6$ NCs were synthesized by the combination of Bi-doping and Te-doping strategies. Details of the reaction scheme are provided in Fig. 1a. The synthesis methodology is established as a generic method to prepare individual Bi$^{3+}$, Te$^{4+}$, and Sb$^{3+}$ doped or dual-doped (Bi$^{3+}$/Te$^{4+}$) Cs$_2$SnCl$_6$ NCs. The as-prepared NCs were finally dispersed in acetone or toluene. Besides, the NCs were well dispersed in N-methylpyrrolidone (NMP) and isopropanol without any deterioration of optical properties and/or quick precipitation. Detailed synthesis method is provided in the Experimental section. A digital image of the blue, yellow, red and white photoemission of Bi$^{3+}$, Te$^{4+}$, and Sb$^{3+}$, and dual (both the Bi$^{3+}$ and Te$^{4+}$) doped Cs$_2$SnCl$_6$ nanocrystals under 365 nm UV lamp is provided in Fig. 1b. The PLQYs of the corresponding emissions were 26.5, 28, <1, and 16.6% under the excitation at 350, 390, 350, and 370 nm, respectively. While an in situ introduction of both Bi$^{3+}$ and Te$^{4+}$ dopants provided a white-light emission as a result of combination of the blue and yellow emissions from the individual dopant centers, analogous white emission was also observed when individual Bi$^{3+}$ and Te$^{4+}$ doped NCs were mixed post-synthetically (Fig. S1a†). Our attempt of in situ preparation of Sb$^{3+}$, Bi$^{3+}$ and Te$^{4+}$ triple-
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ides, except Bi. The coordination of Bi-dopant consists of \([\text{BiCl}_5]\) pyramidal entity plus a Cl vacant substituting the \([\text{SnCl}_6]\) octahedra. The geometry of the Bi–Cl coordination is predicted from a detailed theoretical calculation from a literature report.35

The UV-Vis absorbance spectra of purified Bi\(^{3+}\), Te\(^{4+}\), Bi\(^{3+}/\text{Te}^{4+}\), and Sb\(^{3+}\)-doped \(\text{Cs}_2\text{SnCl}_6\) NCs are presented in Fig. 2a, b, and S2a,† respectively. Bi\(^{3+}\) and Sb\(^{3+}\) doped NCs have deep UV absorption band with a maximum near 340 nm, while Te\(^{4+}\) doped NCs have a double-peak absorption, one peak in the UV region near 300–340 nm, and another one in the near-UV to visible region 380–425 nm. Their characteristic blue, yellow and red photoluminescence (PL), 1-T (where \(T\) is transmittance) and PL excitation (PLE) spectra are presented in Fig. 2c, d and S2b.† We optimized the dopant percentage at 30% of Bi-precursor for the blue-emitter, and 50% of Te-precursor for the yellow-emitter, which provides highest PL intensity, beyond which the PL intensity was nearly saturated. Fig. S3a, b and S2a† provides the PL spectra and PLQYSs of Bi\(^{3+}\) and Te\(^{4+}\) doped \(\text{Cs}_2\text{SnCl}_6\) NCs at different dopant precursor concentrations. The origin of these emissions is from STEs, which is supported by large Stokes shifts and broad emission bandwidths (Table 1). For PL measurements, Bi\(^{3+}\)- and Sb\(^{3+}\)-doped \(\text{Cs}_2\text{SnCl}_6\) NCs were excited at 350 nm, and Te\(^{4+}\)-doped \(\text{Cs}_2\text{SnCl}_6\) NCs were excited at 390 nm. Detailed optical characteristics including absolute PLQYS data are provided in Table 1. These experiments were carried out with NCs dispersed in toluene (or acetone).

Beyond the doping with a single dopant, simultaneous doping with two ions was performed. The synthesis was carried out in situ with the aim of incorporating both the Bi\(^{3+}\) and Te\(^{4+}\) dopants into \(\text{Cs}_2\text{SnCl}_6\) NCs. Herein, we obtained an aggregated white emission from the mixture of blue and yellow emitters. Interestingly, we were able to acquire the white light emission from the one pot reaction of dual-doped (Bi\(^{3+}\) and Te\(^{4+}\)) \(\text{Cs}_2\text{SnCl}_6\) NCs, where no other phase mixing was observed. We optimized the best obtained white-emission from the initial loading of the 30% of Bi-dopant and 50% of Te-dopant precursors. Optical characteristics of white emitting dual-doped Bi/Te-\(\text{Cs}_2\text{SnCl}_6\) NCs are presented in Fig. 3. Fig. 3a presents the PL, 1-T, and PLE spectra of white emissive dual-doped \(\text{Cs}_2\text{SnCl}_6\) NCs. Two different PLE spectra corresponding to PL emissions at 450 nm (blue line) and 570 nm (green line) are presented, corresponding to the PL peak positions produced by Bi\(^{3+}\) and Te\(^{4+}\) dopants, respectively. The overlapping of two PLE spectra determines common excitation spectral region suitable to generate the white light emission (Fig. S4†). The suitable excitation wavelengths in this region for obtaining maximum white emission are found to be at ~340 and 370 nm. The PLE spectrum detected at 500 nm, a wavelength common for both Bi\(^{3+}\) and Te\(^{4+}\) dopant emissions, includes features from both of the dopant centers (Fig. S5†). A variation of Bi and Te-precursor concentrations was carried out to optimize the best white-emission, and their PL spectra are presented in Fig. S6,† and corresponding PLQYSs in Table S3.† Fig. S7† presents the UV-Vis absorbance of dual-doped \(\text{Cs}_2\text{SnCl}_6\) NCs.

**Fig. 1** (a) Schematic presentation of reaction. (b) Digital image of illuminated suspensions of NCs under a 365 nm UV-lamp. Digital images of Bi\(^{3+}\), Te\(^{4+}\), Bi\(^{3+}/\text{Te}^{4+}\), and Sb\(^{3+}\)-doped \(\text{Cs}_2\text{SnCl}_6\) NCs spin-coated on top of a glass substrate under (c) the daylight and (d) a 365 nm UV-lamp. (e) Crystal structure model of \(\text{Cs}_2\text{SnCl}_6\) and the corresponding dopant substitution model.
NCs, which includes the absorption features from both the dopants. Fig. 3b presents a set of PL spectra measured under different excitation wavelength. A ratio of intensities at the maximum points of yellow versus blue emission calculated from Fig. 3b and plotted against excitation wavelength is presented in Fig. 3c, where equal intensities of both the blue and yellow PL, well suited for white emission, comes at ∼340 and 370 nm excitation, with PYQY of 10.6 and 16.6%, respectively. A plot of PLQY versus excitation wavelength is presented in Fig. S8† and shows that PLQY decreased from 340 to 345 nm due to a growth of the blue PL contribution and increases beyond 350 nm due to a growth of the yellow PL contribution. Noteworthy, individual blue-emitting Bi³⁺ doped Cs₂SnCl₆ NCs possessed a PLQY ~26.5% at the excitation wavelength of 350 nm, and the yellow-emitting Te⁴⁺-doped Cs₂SnCl₆ possessed a PLQY of ~28% at the excitation wavelength of 390 nm, while dual doped Cs₂SnCl₆ NCs presents a maximum PLQY of ~18.37%, for an excitation wavelength of 375 nm. When these two ions were doped in situ, it resulted in lower PLQY values, which is possibly due to the reabsorption of some blue light by the yellow emitters. A CIE chromaticity coordinates of the emission spectra (presented in Fig. 3b) are presented in Fig. 3d. At 340 and 370 nm excitation wavelengths, the CCT values are 6113 K and 6160 K, which has a good agreement with the pure white emission. Fig. 3e presents the CIE chromaticity coordinates from the blue, white and yellow emitting NCs in a same plot.

Table 1  Optical characteristics of different metal-ion doped Cs₂SnCl₆ NCs obtained from our synthesis protocol

<table>
<thead>
<tr>
<th>Dopant ion</th>
<th>Excitation wavelength (nm)</th>
<th>PL maximum (nm)</th>
<th>Stokes shift (nm)</th>
<th>FWHM of emission peak (nm)</th>
<th>PLQY (%) (in solution)</th>
<th>Light emission under the UV lamp (365 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi³⁺</td>
<td>350</td>
<td>450</td>
<td>108</td>
<td>80</td>
<td>26.5</td>
<td>Blue</td>
</tr>
<tr>
<td>Te⁴⁺</td>
<td>390</td>
<td>570</td>
<td>160</td>
<td>105</td>
<td>28</td>
<td>Yellow</td>
</tr>
<tr>
<td>Sb⁵⁺</td>
<td>350</td>
<td>650</td>
<td>290</td>
<td>180</td>
<td>&lt;1</td>
<td>Red</td>
</tr>
</tbody>
</table>

NCs presents a maximum PLQY of ~18.37%, for an excitation wavelength of 375 nm. When these two ions were doped in situ, it resulted in lower PLQY values, which is possibly due to the reabsorption of some blue light by the yellow emitters. A CIE chromaticity coordinates of the emission spectra (presented in Fig. 3b) are presented in Fig. 3d. At 340 and 370 nm, it has a coordinate value (0.32, 0.33) and (0.32, 0.32), respectively. Table S3† provides the CIE coordinate values at different Bi and Te dopant percentages at 340 nm excitation from the PL spectra of Fig. S6. Table S4† provides the coordinate values and correlated color temperature (CCT) values under different excitation wavelengths. At 340 and 370 nm excitation wavelengths, the CCT values are 6113 K and 6160 K, which has a good agreement with the pure white emission. Fig. 3e presents the CIE chromaticity coordinates from the blue, white and yellow emitting NCs in a same plot.
FIG. 4 displays a set of XRD patterns of Bi$^{3+}$/Te$^{4+}$ dual-doped (Bi$^{3+}$ and Te$^{4+}$) and undoped Cs$ _2 $SnCl$ _6 $ NCs matched with Cs$ _2 $SnCl$ _6 $ crystal phase with COD: 1010176. These obtained patterns perfectly confirm the formation of phase-pure Cs$ _2 $SnCl$ _6 $ NCs using our generic synthesis method without any dopant-based additional impurity phases. Similar

Fig. 3 (a) PL, PLE and 1-T spectra of Bi$^{3+}$/Te$^{4+}$ dual-doped Cs$ _2 $SnCl$ _6 $ NCs. The excitation wavelength for the PL measurement was 340 nm. PLE spectra were detected at two different emission maximum, 450 nm and 570 nm. (b) A set of PL spectra of dual-doped Cs$ _2 $SnCl$ _6 $ NCs under different excitation wavelengths. (c) Plot of peak intensity ratio of yellow/blue bands vs. the excitation wavelength. (d) CIE chromaticity coordinates (CIE 1931) of dual-doped (Bi$^{3+}$ and Te$^{4+}$)-Cs$ _2 $SnCl$ _6 $ NCs. (e) CIE chromaticity coordinates (CIE 1931) of blue-emitting Bi$^{3+}$ doped Cs$ _2 $SnCl$ _6 $ NCs (0.14, 0.08), white-emitting Bi$^{3+}$ and Te$^{4+}$-doped Cs$ _2 $SnCl$ _6 $ (0.32, 0.33) and yellow-emitting Te$^{4+}$-doped Cs$ _2 $SnCl$ _6 $ (0.39, 0.54) NCs. Corresponding coordinate values and color temperature values are provided in Table S4.†

FIG. 4 (a) XRD patterns of doped and undoped Cs$ _2 $SnCl$ _6 $ NCs. The label of the XRD patterns matched with standard Cs$ _2 $SnCl$ _6 $ (COD: 1010176). (b) Zoomed XRD patterns of (111) peak extracted from Figure 4a and displaying the peak shifting for doped materials towards lower angle as compared to undoped one.

Fig. 4a displays a set of XRD patterns of Bi$^{3+}$, Te$^{4+}$, dual-doped (Bi$^{3+}$ and Te$^{4+}$) and undoped Cs$ _2 $SnCl$ _6 $ NCs matched with Cs$ _2 $SnCl$ _6 $ crystal phase with COD: 1010176. These obtained patterns perfectly confirm the formation of phase-pure Cs$ _2 $SnCl$ _6 $ NCs using our generic synthesis method without any dopant-based additional impurity phases. Similar
XRD pattern of Sb$^{3+}$-doped Cs$_2$SnCl$_6$ NCs is provided in Fig. S9,$^\dagger$ compared with the undoped Cs$_2$SnCl$_6$ and matched with the label of aforementioned Cs$_2$SnCl$_6$ crystal phase. Fig. 4b presents the zoomed XRD patterns of (111) peak extracted from Fig. 4a, which shows a XRD peak shifting towards lower angles. Basically, the shifting originates herein due to the dopant ion induced lattice expansion. A larger shift was observed in case of Bi$^{3+}$-doped and Bi$^{3+}$/Te$^{4+}$-doped Cs$_2$SnCl$_6$ NCs due to the larger ionic radius of Bi$^{3+}$, lesser shift is observed for Te$^{4+}$-doped Cs$_2$SnCl$_6$ NCs. Transmission electron microscopy (TEM) images of as-prepared Bi$^{3+}$-doped Cs$_2$SnCl$_6$, Te$^{4+}$-doped Cs$_2$SnCl$_6$, and Bi$^{3+}$/Te$^{4+}$-doped Cs$_2$SnCl$_6$ are provided in Fig. 5a, c, and e, respectively. TEM images of Sb$^{3+}$-doped Cs$_2$SnCl$_6$ and undoped Cs$_2$SnCl$_6$ NCs are provided in Fig. S10a and b.$^\dagger$ The average particle sizes of Bi$^{3+}$-doped Cs$_2$SnCl$_6$, Te$^{4+}$-doped Cs$_2$SnCl$_6$, and dual-doped (Bi$^{3+}$ and Te$^{4+}$) Cs$_2$SnCl$_6$ are between 50–70 nm.

Table 2 provides the ionic radii of different B-site cations as well as the calculated d-spacings from the HRTEM analysis, from which it was anticipated that incorporation of dopants will lead to the lattice expansion, which caused (i) shifting to lower angles in the XRD patterns, as observed in Fig. 4b, and (ii) increasing the d-spacing. HRTEM analysis of different doped- and undoped-Cs$_2$SnCl$_6$ has been made in order to determine the d-spacing, as pointed out in Table 2. Fig. 5b, d and f provide the HRTEM images, and the FFT with spots from the (111) plane are shown in the inset of HRTEM images. The HRTEM images of Sb$^{3+}$-doped Cs$_2$SnCl$_6$ and undoped

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**Fig. 5** (a, c and e) TEM, (b, d and f) HRTEM, and FT-SAED pattern (inset of b, d and f) of Bi$^{3+}$-doped (a and b), Te$^{4+}$-doped (c and d), and dual doped (e and f) Cs$_2$SnCl$_6$ NCs. Calculated d-spacings of (111) plane are mentioned in figures (b, d and f). Details of the calculated d-spacings are provided in Table 2.
Atoms is higher in 0D A2BX6 in comparison to the well-known the nonpolar end outside whereas the halides (chlorides) are with oleic acid by the carboxylate functional group, keeping into polar solvents for catalytic applications. However, providing the hydrophilicity to the metal halide perovskite NCs are still elusive. Our as-synthesized hydrophilic perovskite NCs could be one of the interests in future for the catalytic applications.

We have incorporated the white-emitting NCs into PMMA with the aim of preparing a composite polymeric film, which allows controlling the loading of the optically active material and serving as a flexible substrate, for broadening the material’s versatility in case the ultimate application demands specific requirements. As shown in Fig. S15, the composite film displays a cold-white emission, resulting from a higher blue and less yellow contribution, upon excitation with 355 nm pulsed light. Thereby, this material could be potentially used, on one hand, as a down-converter by integrating it on an LED chip with emission comprised within 340 and 370 nm to provide a white-light emission, but on the other hand, it could be also exploited as a (bio-)marker or anti-counterfeiting purposes. It is worth mentioning that the small diameter of the NCs is compatible for their deposition by means of printing techniques, e.g. inkjet upon ink formulation and/or 3D-printing once incorporated into liquid resins or plastic filaments, for the development of advanced materials.

For understanding optical PLE and absorption spectra, we performed theoretical calculations of the bulk Bi3+/Te4+-doped Cs2SnCl6, for this purpose “Quantum Espresso”, a computational tool based on density functional theory (DFT), plane waves, and pseudopotentials. With this program, running on a high-performance computer, we have calculated an orthorhombic unit cell of 143 atoms and orthogonal dimensions 10.78 Å, 21.66 Å, and 21.51 Å. The supercell contains the host vacancy-ordered double perovskite, a Bi atom substituting a Sn atom, a Cl vacancy aside (to produce a BiSn + VCl defect complex and a [BiCl5]2− octahedron), and a Te atom substituting another Sn atom (this defect gives [TeCl6]2− octahedrons); the unit cell is drawn in Fig. 6a with indication of point defects. The calculations were performed on the Γ point, using Optimized Norm-Conserving Vanderbilt Pseudopotentials (ONCVPSP) generated with the generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE), and spin–orbit interactions. As simulation of a system with a low doping level as the case analyzed here, see Table S10, requires a significantly long computational time, we consider theoretically a system with higher concentration to decrease the time but obtaining a representative qualitative picture of the density of states created by the doping elements.

Within this ab initio approach, we investigated the lowest-energy optical transitions in the crystal from the valence band into the conduction band based on the calculated densities of states, plotted in Fig. 6a. As concerns these excitations, three selection rules should be considered (set out in the ESI†).
Following these restrictions, the optical transitions in our material would occur between \( sp \)-like impurity levels localized within the band gap, and \( p \)-like empty levels in the conduction band, also contributed by the dopants (see the ESI† for more detail upon these excitations).

In Fig. 6a, the referred \( sp \)-like states appear in the peaks labeled as Te and Bi, and the \( p \)-like empty states are located in the peaks labeled as A, B, and C. The photoexcitation energies extracted from the positions of these peaks qualitatively match and theoretically explain the main experimental peaks observed in PLE and absorption spectra.

Concerning the observed PL spectra, it is worth mentioning that, when the carriers are photo-excited, they produce large distortions in the lattice resulting in a decrease of the exciton energy and therefore its trapping and spatial localization. For this reason, the localized excitations are called self-trapped excitons, which are indeed typically observed in vacancy-ordered double perovskites. These photoinduced distortions result in lowering the energies of both STE-type excited states, see blue wavy lines in Fig. 6b, and thus are responsible for the large Stokes shifts observed in our PL measurements.

4. Conclusion

In summary, a generic synthesis strategy has been developed in order to synthesize ligand-capped metal ion(s) doped \( \text{Cs}_2\text{SnCl}_6 \) NCs that easily can be deposited in thin films. Bi\(^{3+}\), Te\(^{4+}\), and Sb\(^{3+}\) were used as the B-site dopants, which provided the blue, yellow and red emissions, respectively. As an alternative to the visible light emitting lead-halide perovskites, these materials successfully take over the visible emission coverage. As far as we know, this is the first report where Bi\(^{3+}\) and Te\(^{4+}\) doped \( \text{Cs}_2\text{SnCl}_6 \) materials have been synthesized as colloidal NCs with organic capping contrary to previous reports where bulk powders were produced. An \textit{in situ} synthesis or the post synthetic mixing endowed the white-light emission, in which a perfect color mixing of blue and yellow emissions was realized originating from Bi and Te dopants. The CIE chromaticity coordinates support the emission of pure white PL from this material. XRD patterns of the synthesized NCs endorsed the formation of phase-pure doped and undoped \( \text{Cs}_2\text{SnCl}_6 \) NCs. The dopant inclusion was assessed by the XRD peak-shifting due to the lattice expansion caused by the replacement of Sn\(^{4+}\) with the larger sized dopant ions. The NC form allows the easy preparation of thin films by spin coating and, most important, these NC thin films were stable at least over 40 days as per the laboratory reports. Theoretical calculations revealed the incorporation of dopant ions into the \( \text{Cs}_2\text{SnCl}_6 \) matrix at the Sn-site, explaining the absorption properties and STE character of emission. In addition, NCs were dispersed in various polar solvents like isopropanol and NMP without any deterioration of optical properties due to their hydrophilicity, which could be of significant interest for wide applicability.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This project has been partially supported by European Union’s Horizon 2020 Research and Innovation Program under grant agreement no 862656 (project DROP-IT), Ministry of Science and Innovation of Spain under Project STABLE (PID2019-
We acknowledge SCIC from Jaume I University (UJI) for help with XRD characterization. We acknowledge the SCSIE from the University of Valencia for providing TEM facilities.

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