# **PHOTONICS** Research

# Controllable one-step doping synthesis for the white-light emission of cesium copper iodide perovskites

RANRAN FAN, SHAOFAN FANG, CHENGCHUAN LIANG, ZHAOXING LIANG, AND HAIZHE ZHONG\*

International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education, Institute of Microscale Optoelectronics, Shenzhen University, Shenzhen 518060, China \*Corresponding author: haizhe.zhong@szu.edu.cn

Received 13 November 2020; revised 8 February 2021; accepted 19 February 2021; posted 22 February 2021 (Doc. ID 415015); published 21 April 2021

In this paper, a controllable one-step doping method has been successfully adopted in the cesium copper iodide perovskite's luminescence, a high-quality white-light emission with Commission Internationale de l'Eclairage (CIE) coordinates of (0.3397, 0.3325), and a color rendering index (CRI) reaching up to 90 was realized in a convenient way. Through adding impurities into the  $Cs_3Cu_2I_5$  system, high efficiency and stable  $CsCu_2I_3$  was synthesized, and the coexistence of varied high luminescence phases realized the white lighting. Strikingly, blue-emitting  $Cs_3Cu_2I_5$  and yellow-emitting  $CsCu_2I_3$  could coexist, and their respective luminescence was not interacted in the compound, which was beneficial for acquiring a single emission and highly efficient white lighting. This work carried out a deep exploration of the Cu-based metal halides, and would be favorable to the applications of lead-free perovskites. © 2021 Chinese Laser Press

https://doi.org/10.1364/PRJ.415015

## **1. INTRODUCTION**

Halide perovskites are prospective materials for optoelectronics because of the remarkable properties, such as low manufacturing cost, high luminescence efficiency, and tunable light emission characters due to their abundant variety of compositions [1–4]. Among the numerous applications, the white-light emission of organic-inorganic hybrids and all inorganic halide perovskites have received special attention [5–7]. Through flexible regulation of halogen elements in CsPbX<sub>3</sub> (X = Cl, Br, I), the white emission with a diverse color temperature and index can be generated [8,9]. However, the anion exchange derived from mixtures of different halide perovskites, and the relatively narrow coverage of lead (Pb) in halide-based perovskites' luminescent spectra are important factors hindering the development of white lighting [10-12]. Meanwhile, the problems of thermal instability in organic systems and toxicity caused by the heavy Pb limit their further commercial applications [13,14]. In view of this situation, all-inorganic lead-free metal halide perovskites will have more promising prospects in an efficient, stable, and eco-friendly white lighting.

Control of material dimensionality enables them to form various structure types and light emission features [15–17]. The typical 3D and 2D metal halides have been widely investigated because of their excellent optical and electronic characteristics. Nevertheless, low-dimensional 1D and 0D materials

exhibit more unique photophysical properties, such as a large Stokes shift, broadband emission, and high photoluminescence quantum yield (PLQY) due to the self-trapped excitons or excited state structural reorganization [18-20]. Recently, Cubased metal halide perovskites are gradually coming into view because of their abundance, low environmental impact, high efficiency, and low-dimensional structures. For instance, green emission CsCuCl<sub>3</sub> and Cs<sub>2</sub>CuCl<sub>4</sub> nanocrystals [21], bluegreen luminescence Cs<sub>2</sub>CuX<sub>4</sub> (X = Cl, Br, Br/I) perovskite quantum dots [22], blue light emission  $Cs_3Cu_2Br_{5-x}I_x$  $(0 \le x \le 5)$  with near-unity PLQY [23], and CsCu<sub>2</sub>X<sub>3</sub> (X = Cl, Br, I) with improved air and thermal stability [24] have been recently reported. Specifically, Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> with a 0D electronic structure, large Stokes shift, and strong blue emission has been fabricated and applied for LED devices [25,26]. Another phase of cesium copper iodide, CsCu<sub>2</sub>I<sub>3</sub>, shows broadband yellow emission [24], and the stable yellow LED based on it was successfully realized [27]. Additionally, CsCu<sub>2</sub>I<sub>3</sub> single crystals with a high-PLQY due to strongly localized 1D excitonic recombination have been reported [28]. As both Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> and CsCu<sub>2</sub>I<sub>3</sub> are pure iodide phases, the general mixed halide's exchange existing in perovskite's mixtures could be avoided, and pure white emission can be further achieved by appropriate mixing of these phases. Previously, a pure whitelight emission has been successfully realized by adjusting the appropriate mixing ratio of these two phases [29,30]. Nevertheless, these methods always needed to fabricate two pure phases of blue emission  $Cs_3Cu_2I_5$  and yellow emission  $CsCu_2I_3$ , and then precisely control the mixing ratio of these individual luminescent materials, which was intricate and inconvenient for the practical application. Therefore, developing a simple intrinsic white-light emission of a cesium copper iodide system will become an effective approach. It has been reported that through a controllable CsI–CuI phase transformation by solvent treatment, stable CsCu<sub>2</sub>I<sub>3</sub> was obtained from Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>, and a single white-emission layer could be prepared [31]. In addition, Shi's group has reported the electroluminescent white-light emitting diodes in terms of Cu-based halide materials [32].

In this paper, we have successfully prepared the white luminescent material by a one-step doping method, achieving full coverage of the visible spectrum. Through adding impurities into the  $Cs_3Cu_2I_5$  system, high efficiency and stable  $CsCu_2I_3$ was successfully synthesized, and the coexistence of varied high luminescence phases realized the white lighting. By means of the disposable preparation of  $Cs_3Cu_2I_5$  and  $CsCu_2I_3$  phases, a high-quality and more uniform white luminescence with CIE coordinates of (0.3397, 0.3325) and a CRI reaching 90 could be generated in a simple way.

#### 2. MATERIALS AND METHODS

Cesium iodide (CsI, 99.9%), copper (I) iodide (CuI, 99.999%), neodymium iodide (NdI<sub>3</sub>, 99.9%), terbium iodide (TbI<sub>3</sub>, 99.99%), praseodymium iodide (PrI<sub>3</sub>, 99.9%), bismuth iodide (BiI<sub>3</sub>, 99.9%), N, N-dimethylformamide (DMF, 99.9%), and isopropanol (99.5%) were directly used without further purification.

The cesium copper iodide perovskites were synthesized via an antisolvent infiltration method, which was performed at room temperature by adding the precursor solution within a good solvent into a nonpolar poor solvent. The blend of two various solvents induced a transient supersaturation, leading to the nucleation and form of perovskites. Cesium iodide, copper (I) iodide, and impurity materials (in this paper, NdI<sub>3</sub>, TbI<sub>3</sub>, PrI<sub>3</sub>, and BiI<sub>3</sub> were used as impurities, respectively) in different molar ratios were firstly dissolved in DMF to get a precursor solution. Then, the solution was rapidly dropped into the antisolvent of isopropanol to form a precipitate, and the resulting products were the mixture of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> and CsCu<sub>2</sub>I<sub>3</sub>. With the increase in the molar ratio of doping materials, a mixture with different proportions of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> and CsCu<sub>2</sub>I<sub>3</sub> could be obtained. The specific synthesis procedures are as below.

Adding NdI<sub>3</sub> into the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> system. In the synthesis of molar ratios of 9 mol%, CsI (0.6 mmol), CuI (0.364 mmol), and NdI<sub>3</sub> (0.036 mmol) were dissolved in DMF (4 mL). The mixture was stirred for 2 h at 80°C, then we let it cool naturally to room temperature. Next the precursor solution was rapidly added into isopropanol (20 mL) with vigorous stirring under air ambient at room temperature, and a precipitate was produced immediately during this process. Then, the resulting precipitate was filtered and washed with isopropanol; the yield of the product was about 75%. The other three concentrations

were obtained by three corresponding molar doses: 3 mol% (0.6 mmol CsI, 0.388 mmol CuI, and 0.012 mmol NdI<sub>3</sub>), 5 mol% (0.6 mmol CsI, 0.38 mmol CuI, and 0.02 mmol NdI<sub>3</sub>), and 7 mol% (0.6 mmol CsI, 0.372 mmol CuI, and 0.028 mmol NdI<sub>3</sub>).

Adding TbI<sub>3</sub>, PrI<sub>3</sub>, and BiI<sub>3</sub> into a Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> system. The impurities were chosen as 9 mol% (0.6 mmol CsI, 0.364 mmol CuI, and 0.036 mmol for TbI<sub>3</sub>, PrI<sub>3</sub>, and BiI<sub>3</sub>, respectively); the synthesis process was the same as above.

Adding  $NdI_3$  into the  $CsCu_2I_3$  system. The impurities were chosen as 9 mol% (0.3 mmol CsI, 0.546 mmol CuI, and 0.054 mmol NdI<sub>3</sub>), and the synthesis process was the same as above.

Synthesis of pure  $Cs_3Cu_2I_5$ : 0.6 mmol CsI and 0.4 mmol CuI were used; the synthesis process was the same as above.

Synthesis of pure  $CsCu_2I_3$ : 0.3 mmol CsI and 0.6 mmol CuI were used; the synthesis process was the same as above.

Photoluminescence (PL), photoluminescence excitation (PLE), and photoluminescence quantum yield (PLQY) measurements were performed at ambient temperature by an FS5 fluorescence spectrometer equipped with a xenon lamp and an integrating sphere. Powder X-ray diffraction (PXRD) measurements were performed by the Rigaku MiniFlex600 system equipped with a Cu-Kα radiation source  $(\lambda = 1.5418 \ \mu m)$ . All scans were performed at room temperature with a step size of 0.02°. X-ray photoelectron spectroscopy (XPS) analyses were conducted using an ESCALAB 250Xi spectrometer. Scanning electron microscope (SEM) measurements were performed by a ZEISS SUPRA 55 from Carl Zeiss, Germany. High resolution transmission electron microscopy (HRTEM) images were measured by the JEM-3200FS (JEOL).

### 3. RESULTS AND DISCUSSION

The Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> system with added NdI<sub>3</sub> is first detected by the SEM and TEM techniques. The SEM image [Fig. 1(a)] implies the large quantity and good uniformity of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> and CsCu<sub>2</sub>I<sub>3</sub> phases. Energy-dispersive X-ray spectroscopy (EDS) mapping [Fig. 1(b)] confirms that Cs, Cu, I, and Nd are evenly distributed in the material. The SEM and TEM [Fig. 1(c)] images of the as-synthesized Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> and CsCu<sub>2</sub>I<sub>3</sub> composites show a dual-phase morphology characteristic composed of nanoparticles and nanorods, which correspond to Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> and CsCu<sub>2</sub>I<sub>3</sub>, respectively. Such morphology features can effectively avoid the color changes of the composites caused by anion exchange, because the two components exist individually without the formation of compact structure configuration, which will make it quite fit to emit stable white light. The TEM image [Fig. 1(c)] shows the micro morphologies of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> and CsCu<sub>2</sub>I<sub>3</sub>, in which Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> crystallizes as nanoparticles with an average diameter of ~300 nm, whereas  $C_{s}Cu_{2}I_{3}$  appears as nanorods with the average length of ~2  $\mu$ m and width of ~450 nm. The TEM lattice fringes and fast Fourier transform (FFT) images of d-spacing ~3.24 Å and  $\sim 2.1$  Å (1 Å = 0.1 nm) coincide with the lattice planes of (213) and (350) for  $Cs_3Cu_2I_5$  and  $CsCu_2I_3$ , respectively [Figs. 1(d) and 1(e)]. The X-ray photoelectron spectroscopy (XPS) measurements are conducted to validate the chemical



**Fig. 1.** (a) SEM, (b) EDS mapping, and (c) TEM images of the sample with NdI<sub>3</sub>. The lattice planes and fast Fourier transform (FFT) images of (d)  $Cs_3Cu_2I_5$  nanoparticles and (e)  $CsCu_2I_3$  nanorods. (f) XPS analysis of the sample with 9 mol% NdI<sub>3</sub>, and the respective spectra of (g) Cs 3d, (h) Cu 2p, and (i) I 3d.

states of ions [Figs. 1(f)–1(i)]. The binding energies of 951.8 eV and 932 eV coincide to Cu  $2p_{1/2}$  and Cu  $2p_{3/2}$ , respectively, which demonstrates the monovalent state for copper in the material. Meanwhile, Cs 3d and I 3d correspond to the +1 and -1 states, which are consistent with published data for cesium copper iodides [25,29]. These results indicate that a system including both high quality Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> and CsCu<sub>2</sub>I<sub>3</sub> has been successfully prepared through the doping method.

Figure 2(a) demonstrates the PL (photoluminescence) spectra of pure  $Cs_3Cu_2I_5$  and  $CsCu_2I_3$ , in which  $Cs_3Cu_2I_5$  nanoparticles exhibit blue luminescence at 446 nm with a broad FWHM (full width at half maximum) of about 80 nm, while

CsCu<sub>2</sub>I<sub>3</sub> nanorods display yellow emitting at 576 nm with an FWHM of approximately 120 nm. Both samples show large Stokes shifts, and in this way self-absorption by the system can be efficiently prevented. The emissions are possible mostly owing to the self-trapped excitons, deriving from the Jahn-Teller distortion or strong exciton-phonon coupling [23,33]. In addition, broad emissions are usually helpful for enhancing the CRI of white lighting. The PLQYs are ~69.94% for pure Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> and 9.91% for CsCu<sub>2</sub>I<sub>3</sub>, respectively, and the higher PLQY of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> nanoparticles than CsCu<sub>2</sub>I<sub>3</sub> nanorods may result from the stronger exciton binding energy in 0D Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>. The PL spectra of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> system with various



**Fig. 2.** (a) PL spectra of pure  $C_{s_3}Cu_2I_5$  and  $C_sCu_2I_3$ . (b) PL spectra of samples with different concentration of NdI<sub>3</sub> under excitation of 316 nm. (c) PLE spectra of emission peaks corresponding to  $C_{s_3}Cu_2I_5$  and  $C_sCu_2I_3$  of the sample with 9 mol% NdI<sub>3</sub>. (d) CIE coordinates of the sample with 9 mol% NdI<sub>3</sub>. (e) XRD diffraction patterns of samples with different concentration of NdI<sub>3</sub> compared to the standard XRD patterns of  $C_{s_3}Cu_2I_5$  and  $C_sCu_2I_5$ .



Fig. 3. Crystal structures of (a)  $Cs_3Cu_2I_5$  and (b)  $CsCu_2I_3$  with optimized lattice parameters from the top.

ratios of NdI<sub>3</sub> under excitation of 316 nm are shown in Fig. 2(b). At the ratio of 3 mol%, a PL emission involving both Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> and CsCu<sub>2</sub>I<sub>3</sub> has been detected in the material. With the increase of molar ratios, the intensity difference between the emission of CsCu<sub>2</sub>I<sub>3</sub> and Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> diminishes, indicating that the proportion of CsCu<sub>2</sub>I<sub>3</sub> gradually increases. As Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> and CsCu<sub>2</sub>I<sub>3</sub> possess comprehensive red, green, and blue components, a mixture of them could form a white lighting. When the intensities of yellow emission from CsCu<sub>2</sub>I<sub>3</sub> and blue emission from Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> reach an almost equal ratio, a normal white lighting can be produced. From Fig. 2(b), it can be seen that at the ratio of 9 mol%, a white emission has been successfully formed. Figure 2(d) shows that the CIE coordinates of it are (0.3397, 0.3325), approaching the standard white light of (0.33, 0.33). In addition, the CRI of this material can reach up to 90 and its PLQY is 16.9%. The PLE (photoluminescence excitation) spectrum for the sample with concentration of 9 mol% is shown in Fig. 2(c). It can be seen that under the excitation wavelength of 316 nm, the PLE efficiency for CsCu<sub>2</sub>I<sub>3</sub> and Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> is almost the same, indicating that a white emission can be motivated at this wavelength, which is consistent with the 9 mol% white PL spectra in Fig. 2(b). Apparently, at this wavelength both of the PL efficiencies for  $C_{s}Cu_{2}I_{3}$  and  $C_{s_{3}}Cu_{2}I_{5}$  do not reach the optimum, but the yellow emission from CsCu<sub>2</sub>I<sub>3</sub> and blue emission from Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> reach a balance, and a normal white emission can be produced. Figure 2(c) also demonstrates that although the PLQY of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> is much higher than that of CsCu<sub>2</sub>I<sub>3</sub>, only the PL efficiency of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>, which has the same amount as that of CsCu<sub>2</sub>I<sub>3</sub>, will be effective enough to make a contribution to the form of white lighting. As a result, the emitting intensities will nearly achieve a balance. The large amount of  $CsCu_2I_3$  in the material with the ratio of 9 mol% will lead to the increase of the balanced effective PL efficiency and the overall powerful white luminescence. To further investigate how the doping ratios influence the formation of CsCu<sub>2</sub>I<sub>3</sub> and the proportion between Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> and CsCu<sub>2</sub>I<sub>3</sub>, the XRD results are shown in Fig. 2(e). At the low ratio of 3 mol%, the corresponding diffraction peaks of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> and CsCu<sub>2</sub>I<sub>3</sub> appear simultaneously, indicating that both of the two phases are synthesized in the material. Meanwhile, the weak peak intensity of CsCu<sub>2</sub>I<sub>3</sub> signifies that the proportion of it is tiny compared to another phase of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>. With the increase of dopant, the diffraction peak of CsCu<sub>2</sub>I<sub>3</sub> is enhanced, while the diffraction

from  $Cs_3Cu_2I_5$  is gradually weakened, which means that the amount of  $CsCu_2I_3$  increases accordingly. This result is consistent with the PL spectra [Fig. 2(b)], along with the increase of the doping molar ratio, and the PL intensity difference between emission of  $CsCu_2I_3$  and  $Cs_3Cu_2I_5$  gradually diminishes.

It has been reported that Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> crystallizes in the *Pnma* space group of an orthorhombic crystal system. Two types of  $Cu^+$  appear as tetrahedral sites of  $Cu^+I_4$  and triangular sites of  $Cu^+I_3$  in the material, which are edge-connected coming into the isolated [Cu<sub>2</sub>I<sub>5</sub>]<sup>3-</sup> units [34,35]. In particular, these units are divided by the nearby Cs<sup>+</sup> ions, forming a zero-dimensional structure [Fig. 3(a)]. In contrast, CsCu<sub>2</sub>I<sub>3</sub> crystallizes in the Cmcm space group of an orthorhombic system, in which Cu<sup>+</sup>I<sub>4</sub> tetrahedra sites share common faces and edges and form double chains of  $Cu_2I_3$  along the *c*-axis separated by cesium, leading to a 1D structure [Fig. 3(b)]. In the research of lead bromine perovskite, it has been reported that CsPbBr3 can gradually transform into another phase of Cs<sub>4</sub>PbBr<sub>6</sub> by adding ZnBr<sub>2</sub> as a revulsive. The process of "survival of the fittest" occurs in CsPbBr<sub>3</sub>, in which the good quality and stable CsPbBr<sub>3</sub> is retained, while the unstable CsPbBr<sub>3</sub> is decomposed and likely ripened into the 416-structure by adding the  $ZnBr_2$  revulsive [36]. Like the role of  $ZnBr_2$  in the system of Cs-Pb-Br, the mechanism of the doping process in the transformation of CsCu<sub>2</sub>I<sub>3</sub> and Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> can be attributed to the role the impurities played as a conversion revulsive. The 1D CsCu<sub>2</sub>I<sub>3</sub> is more stable and easier to generate than the 0D  $Cs_3Cu_2I_5$ . When the dopants are added into the  $Cs_3Cu_2I_5$  system, the balance of the whole system will be destroyed, in this process the stable Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> nanocrystals are retained, while the unstable particles with poor quality will be disintegrated and rapidly formed into the CsCu<sub>2</sub>I<sub>3</sub> structure. The resulting mixture of these two phases can be obtained on this basis. However, when the circumstance is in reverse, namely materials are added into the CsCu<sub>2</sub>I<sub>3</sub> system, another phase of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> does not appear simultaneously (Fig. 4). It can be seen that in every doping concentration, only PL and XRD peaks of CsCu<sub>2</sub>I<sub>3</sub> and undissolved CuI (PL emission of 420 nm) exist in the material. The form of nanocrystals requires that the precursor concentration exceeds the critical concentration of nucleation, and a large number of nuclei occur in a very short period of time. When precursor concentration is lower, the nanoparticles will dissolve and disappear, and thus the 0D Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> cannot form concurrently in the CsCu<sub>2</sub>I<sub>3</sub> system by the doping method.

Next, other materials like TbI<sub>3</sub>, PrI<sub>3</sub>, and BiI<sub>3</sub> were added in turn to measure their respective effect on the white emission efficiency. As shown in Fig. 5(a), PL white spectra involving  $Cs_3Cu_2I_5$  and  $CsCu_2I_3$  peaks have been detected in every material. The PLQYs for NdI<sub>3</sub>, TbI<sub>3</sub>, PrI<sub>3</sub>, and BiI<sub>3</sub> are 16.9%, 14.5%, 9.32%, and 5.52%, respectively. The CIE coordinates in the system of NdI<sub>3</sub> and TbI<sub>3</sub> are (0.3397, 0.3325) and (0.3477, 0.3368), respectively [Fig. 5(c)], indicating that white emission has been successfully formed within them. As shown in Fig. 5(b), the corresponding XRD peaks of  $Cs_3Cu_2I_5$ and  $CsCu_2I_3$  appear simultaneously but with different proportions in these samples. Compared to other impurities, the NdI<sub>3</sub> sample has the strongest  $CsCu_2I_3$  in it. In the reaction process, the

Research Article



**Fig. 4.** (a) PL spectra under excitation wavelength of 320 nm. (b) XRD patterns of the samples with  $NdI_3$  added into the  $CsCu_2I_3$  system with various ratios.

solubility and the ionic activity of impurities in the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> precursor solution will affect the amount and quality of CsCu<sub>2</sub>I<sub>3</sub> to a large extent and will further influence the overall luminescence effect. The inset of Fig. 5(a) shows the NdI<sub>3</sub>, TbI<sub>3</sub>, and PrI<sub>3</sub> doped Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> solution. It can be seen that the NdI<sub>3</sub> sample is completely dissolved and more clarified than others, while the TbI<sub>3</sub> and PrI<sub>3</sub> samples are like a suspension similar to colloid, which means that these two impurities do not dissolve absolutely in the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> solution. In addition, Nd is one of the liveliest rare earth metals; it will quickly react in hot solution which is effective to the fast formation of CsCu<sub>2</sub>I<sub>3</sub> and makes positive influence on the overall emission efficiency. Therefore, compared to other dopants, the NdI<sub>3</sub> sample has the strongest CsCu<sub>2</sub>I<sub>3</sub> diffraction peak, indicating the largest amount of CsCu<sub>2</sub>I<sub>3</sub> in it. As discussed previously in Fig. 2, the more amount of CsCu<sub>2</sub>I<sub>3</sub> is beneficial to obtain stronger white emission, and thus the PLQY of the NdI<sub>3</sub> sample is higher than that of other materials. Moreover, the uniformity and quality of the sample could also affect the whole luminescence intensity. The SEM images are shown

in Figs. 5(d)-5(g); the uniformity and quality of  $Cs_3Cu_2I_5$ and  $CsCu_2I_3$  in the NdI<sub>3</sub> sample are much better compared to others, corresponding to its higher PL efficiency. In addition, the new generated material is another factor affecting the PLQY. From Fig. 5(b), it can be found that in the BiI<sub>3</sub>-doped sample new  $Cs_3Bi_2I_9$  appears. It consumes a great deal of Cs and I ions which will compose  $Cs_3Cu_2I_5$  and  $CsCu_2I_3$ , resulting in the whole material getting few effective luminous centers for white emission and a low PL intensity. Therefore, combined with the above factors, the PLQY of the NdI<sub>3</sub> sample is higher than that of other doping materials.

#### 4. CONCLUSIONS

In conclusion, a controllable one-step doping method was adopted in the cesium copper iodide perovskite's luminescence, and the results indicated that a system including  $Cs_3Cu_2I_5$  and  $CsCu_2I_3$  with high quality had been successfully prepared. Through comparing the PL efficiency of samples under various molar ratios and materials, it has been investigated that the



**Fig. 5.** (a) PL spectra of samples with 9 mol% concentration of NdI<sub>3</sub> (PL excitation of 316 nm), TbI<sub>3</sub> (PL excitation of 317 nm), PrI<sub>3</sub> (PL excitation of 319 nm), and BiI<sub>3</sub> (PL excitation of 308 nm). Inset: the precursor solution of NdI<sub>3</sub>, TbI<sub>3</sub>, and PrI<sub>3</sub> samples. (b) XRD patterns of samples with 9 mol% concentration of NdI<sub>3</sub>, TbI<sub>3</sub>, PrI<sub>3</sub>, and BiI<sub>3</sub>. (c) CIE coordinates of samples with 9 mol% NdI<sub>3</sub> and TbI<sub>3</sub>. (d)–(g) SEM images of the samples with 9 mol% NdI<sub>3</sub>, TbI<sub>3</sub>, PrI<sub>3</sub>, and BiI<sub>3</sub>, respectively.

amount of  $CsCu_2I_3$  combining with the uniformity and quality of  $Cs_3Cu_2I_5$  and  $CsCu_2I_3$  was the key factor affecting the white-lighting. Therefore, a high-quality white-emission with CIE coordinates of (0.3397, 0.3325) and CRI of 90 was obtained in a convenient way. This work provides a new approach for the investigation of Cu-based metal halide perovskites and will be helpful for the exploration of lead-free perovskites.

**Funding.** Natural Science Foundation of Guangdong Province (2020A1515010541); Science and Technology Project of Shenzhen (JCYJ20180305124930169, JCYJ20190808143419622, ZDSYS201707271014468).

**Disclosures.** The authors declare no conflicts of interest.

#### REFERENCES

- A. Dutta, R. K. Behera, P. Pal, S. Baitalik, and N. Pradhan, "Near-unity photoluminescence quantum efficiency for all CsPbX<sub>3</sub> (X=Cl, Br and I) perovskite nanocrystals: a generic synthesis approach," Angew. Chem. **131**, 5608–5612 (2019).
- R. J. Sutton, G. E. Eperon, L. Miranda, E. S. Parrott, B. A. Kamino, J. B. Patel, M. T. Hörantner, M. B. Johnston, A. A. Haghighirad, D. T. Moore, and H. J. Snaith, "Bandgap-tunable cesium lead halide perovskites with high thermal stability for efficient solar cells," Adv. Energy Mater. 6, 1502458 (2016).
- Z.-K. Tan, R. S. Moghaddam, M. L. Lai, P. Docampo, R. Higler, F. Deschler, M. Price, A. Sadhanala, L. M. Pazos, D. Credgington, F. Hanusch, T. Bein, H. J. Snaith, and R. H. Friend, "Bright light-emitting diodes based on organometal halide perovskite," Nat. Nanotechnol. 9, 687–692 (2014).
- C. Zhou, Y. Tian, Z. Yuan, H. Lin, B. Chen, R. Clark, T. Dilbeck, Y. Zhou, J. Hurley, J. Neu, T. Besara, T. Siegrist, P. Djurovich, and B. Ma, "Highly efficient broadband yellow phosphor based on zerodimensional tin mixed-halide perovskite," ACS Appl. Mater. Interfaces 9, 44579–44583 (2017).
- E. P. Yao, Z. Yang, L. Meng, P. Sun, S. Dong, Y. Yang, and Y. Yang, "High-brightness blue and white LEDs based on inorganic perovskite nanocrystals and their composites," Adv. Mater. 29, 1606859 (2017).
- Z. Yuan, C. Zhou, Y. Tian, Y. Shu, J. Messier, J. C. Wang, L. J. van de Burgt, K. Kountouriotis, Y. Xin, E. Holt, K. Schanze, R. Clark, T. Siegrist, and B. Ma, "One-dimensional lead halide perovskites with bluish white-light emission," Nat. Commun. 8, 14051 (2017).
- C.-Y. Chang, A. N. Solodukhin, S.-Y. Liao, K. P. O. Mahesh, C.-L. Hsu, S. A. Ponomarenko, Y. N. Luponosov, and Y.-C. Chao, "Perovskite white light-emitting diodes based on a molecular blend perovskite emissive layer," J. Mater. Chem. C 7, 8634–8642 (2019).
- L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. Hendon, R. X. Yang, A. Walsh, and M. V. Kovalenko, "Nanocrystals of cesium lead halide perovskites (CsPbX<sub>3</sub>, X = Cl, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut," Nano Lett. **15**, 3692–3696 (2015).
- Q. A. Akkerman, V. D'Innocenzo, S. Accornero, A. Scarpellini, A. Petrozza, M. Prato, and L. Manna, "Tuning the optical properties of cesium lead halide perovskite nanocrystals by anion exchange reactions," J. Am. Chem. Soc. **137**, 10276–10281 (2015).
- P. Vashishtha and J. E. Halpert, "Field-driven ion migration and color instability in red-emitting mixed halide perovskite nanocrystal lightemitting diodes," Chem. Mater. 29, 5965–5973 (2017).
- M. C. Brennan, S. Draguta, P. V. Kamat, and M. Kuno, "Light-induced anion phase segregation in mixed halide perovskites," ACS Energy Lett. 3, 204–213 (2018).
- G. Nedelcu, L. Protesescu, S. Yakunin, M. I. Bodnarchuk, M. J. Grotevent, and M. V. Kovalenko, "Fast anion-exchange in highly luminescent nanocrystals of cesium lead halide perovskites (CsPbX<sub>3</sub>, X = Cl, Br, I)," Nano lett. **15**, 5635–5640 (2015).
- J. A. Sichert, Y. Tong, N. Mutz, M. Vollmer, S. Fischer, K. Z. Milowska, R. Garcia Cortadella, B. Nickel, C. Cardenas-Daw, J. K. Stolarczyk,

A. S. Urban, and J. Feldmann, "Quantum size effect in organometal halide perovskite nanoplatelets," Nano Lett. **15**, 6521–6527 (2015).

- A. Babayigit, D. D. Thanh, A. Ethirajan, J. Manca, M. Muller, H.-G. Boyen, and B. Conings, "Assessing the toxicity of Pb-and Sn-based perovskite solar cells in model organism Danio rerio," Sci. Rep. 6, 18721 (2016).
- H. Yang, Y. Zhang, J. Pan, J. Yin, O. M. Bakr, and O. F. Mohammed, "Room-temperature engineering of all-inorganic perovskite nanocrystals with different dimensionalities," Chem. Mater. 29, 8978–8982 (2017).
- J. Li, H. Dong, B. Xu, S. Zhang, Z. Cai, J. Wang, and L. Zhang, "CsPbBr<sub>3</sub> perovskite quantum dots: saturable absorption properties and passively Q-switched visible lasers," Photon. Res. 5, 457–460 (2017).
- P. Cheng, L. Sun, L. Feng, S. Yang, Y. Yang, D. Zheng, Y. Zhao, Y. Sang, R. Zhang, D. Wei, W. Deng, and K. Han, "Colloidal synthesis and optical properties of all-inorganic low-dimensional cesium copper halide nanocrystals," Angew. Chem. 58, 16087–16091 (2019).
- K. Sim, T. Jun, J. Bang, H. Kamioka, J. Kim, H. Hiramatsu, and H. Hosono, "Performance boosting strategy for perovskite light-emitting diodes," Appl. Phys. Rev. 6, 031402 (2019).
- M. I. Saidaminov, J. Almutlaq, S. Sarmah, I. Dursun, A. A. Zhumekenov, R. Begum, J. Pan, N. Cho, F. Mohammed, and O. M. Bakr, "Pure Cs<sub>4</sub>PbBr<sub>6</sub>: highly luminescent zero-dimensional perovskite solids," ACS Energy Lett. 1, 840–845 (2016).
- X.-X. Feng, X.-D. Lv, Q. Liang, J. Cao, and Y. Tang, "Diammonium porphyrin-induced CsPbBr<sub>3</sub> nanocrystals to stabilize perovskite films for efficient and stable solar cells," ACS Appl. Mater. Interfaces 12, 16236–16242 (2020).
- E. P. Booker, J. T. Griffiths, L. Eyre, C. Ducati, N. C. Greenham, and N. J. L. K. Davis, "Synthesis, characterization, and morphological control of Cs<sub>2</sub>CuCl<sub>4</sub> nanocrystals," J. Phys. Chem. C **123**, 16951–16956 (2019).
- P. Yang, G. Liu, B. Liu, X. Liu, Y. Lou, J. Chen, and Y. Zhao, "All-inorganic Cs<sub>2</sub>CuX<sub>4</sub> (X = Cl, Br, and Br/l) perovskite quantum dots with blue-green luminescence," Chem. Commun. 54, 11638–11641 (2018).
- 23. R. Roccanova, A. Yangui, H. Nhalil, H. Shi, M.-H. Du, and B. Saparov, "Near-unity photoluminescence quantum yield in blue-emitting  $Cs_3Cu_2Br_{5-x}I_x$  (0  $\leq x \leq$  5)," ACS Appl. Electron. Mater. **1**, 269–274 (2019).
- R. Roccanova, A. Yangui, G. Seo, T. D. Creason, Y. Wu, D. Y. Kim, M.-H. Du, and B. Saparov, "Bright luminescence from nontoxic CsCu<sub>2</sub>X<sub>3</sub> (X= CI, Br, I)," ACS Mater. Lett. 1, 459–465 (2019).
- L. Xie, B. Chen, F. Zhang, Z. Zhao, X. Wang, L. Shi, Y. Liu, L. Huang, R. Liu, B. Zou, and Y. Wang, "Highly luminescent and stable leadfree cesium copper halide perovskite powders for UV-pumped phosphor-converted light-emitting diodes," Photon. Res. 8, 768–775 (2020).
- 26. Y. Li, P. Vashishtha, Z. Zhou, Z. Li, S. B. Shivarudraiah, C. Ma, J. Liu, K. S. Wong, H. Su, and J. E. Halpert, "Room temperature synthesis of stable, printable Cs<sub>3</sub>Cu<sub>2</sub>X<sub>5</sub> (X = I, Br/I, Br, Br/CI, CI) colloidal nanocrystals with near-unity quantum yield green emitters (X = CI)," Chem. Mater. 32, 5515–5524 (2020).
- Z. Ma, Z. Shi, C. Qin, M. Cui, D. Yang, X. Wang, L. Wang, X. Ji, X. Chen, J. Sun, D. Wu, Y. Zhang, X. J. Li, L. Zhang, and C. Shan, "Stable yellow light-emitting devices based on ternary copper halides with broadband emissive self-trapped excitons," ACS Nano 14, 4475– 4486 (2020).
- R. Lin, Q. Guo, Q. Zhu, Y. Zhu, W. Zheng, and F. Huang, "All-inorganic CsCu<sub>2</sub>I<sub>3</sub> single crystal with high-PLQY (≈15.7%) intrinsic white-light emission via strongly localized 1D excitonic recombination," Adv. Mater. **31**, 1905079 (2019).
- P. Vashishtha, G. V. Nutan, B. E. Griffith, Y. Fang, D. Giovanni, M. Jagadeeswararao, T. C. Sum, N. Mathews, S. G. Mhaisalkar, J. V. Hanna, and T. Wu, "Cesium copper iodide tailored nanoplates and nanorods for blue, yellow, and white emission," Chem. Mater. 31, 9003–9011 (2019).
- S. Fang, Y. Wang, H. Li, F. Fang, K. Jiang, Z. Liu, H. Li, and Y. Shi, "Rapid synthesis and mechanochemical reactions of cesium copper

halides for convenient chromaticity tuning and efficient white light emission," J. Mater. Chem. C 8, 4895–4901 (2020).

- S. Liu, Y. Yue, X. Zhang, C. Wang, G. Yang, and D. Zhu, "A controllable and reversible phase transformation between all-inorganic perovskites for white light emitting diodes," J. Mater. Chem. C 8, 8374–8379 (2020).
- Z. Ma, Z. Shi, D. Yang, Y. Li, F. Zhang, L. Wang, X. Chen, D. Wu, Y. Tian, Y. Zhang, L. Zhang, X. Li, and C. Shan, "High color-rendering index and stable white light-emitting diodes by assembling two broadband emissive self-trapped excitons," Adv. Mater. 33, 2001367 (2021).
- J. Luo, X. Wang, S. Li, J. Liu, Y. Guo, G. Niu, L. Yao, Y. Fu, L. Gao, Q. Dong, C. Zhao, M. Leng, F. Ma, W. Liang, L. Wang, S. Jin, J. Han, L. Zhang, J. Etheridge, J. Wang, Y. Yan, E. H. Sargent, and J. Tang,

"Efficient and stable emission of warm-white light from lead-free halide double perovskites," Nature **563**, 541–545 (2018).

- 34. S. Hull and P. Berastegui, "Crystal structures and ionic conductivities of ternary derivatives of the silver and copper monohalides—II: ordered phases within the (AgX)<sub>x</sub>-(MX)<sub>1x</sub> and (CuX)<sub>x</sub>-(MX)<sub>1x</sub> (M = K, Rb and Cs; X=Cl, Br and I) systems," J. Solid State Chem. **177**, 3156–3173 (2004).
- T. Jun, K. Sim, S. limura, M. Sasase, H. Kamioka, J. Kim, and H. Hosono, "Lead-free highly efficient blue-emitting Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> with 0D electronic structure," Adv. Mater. **30**, 1804547 (2018).
- Y. Su, Q. Zeng, X. Chen, W. Ye, L. She, X. Gao, Z. Rena, and X. Li, "Highly efficient CsPbBr<sub>3</sub> perovskite nanocrystals induced by structure transformation between CsPbBr<sub>3</sub> and Cs<sub>4</sub>PbBr<sub>6</sub> phases," J. Mater. Chem. C 7, 7548–7553 (2019).