Highly luminescent and stable lead-free cesium copper halide perovskite powders for UV-pumped phosphor-converted light-emitting diodes

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Received 14 January 2020; revised 20 February 2020; accepted 10 March 2020; posted 13 March 2020 (Doc. ID 387707); published 6 May 2020

Lead halide perovskites have drawn extensive attention over recent decades owing to their outstanding photoelectric performances. However, their toxicity and instability are big issues that need to be solved for further commercialization. Herein, we adopt a facile dry ball milling method to synthesize lead-free $\text{Cs}_3\text{Cu}_2\text{X}_5$ (X = I, Cl) perovskites with photoluminescence (PL) quantum yield up to 60%. The optical features including broad emission spectrum, large Stokes shift, and long PL lifetime can be attributed to self-trapped exciton recombination. The as-synthesized blue emissive $\text{Cs}_3\text{Cu}_2\text{I}_5$ and green emissive $\text{Cs}_3\text{Cu}_2\text{Cl}_5$ lead-free perovskite powders have good thermal stability and photostability. Furthermore, UV-pumped phosphor-converted light-emitting diodes were obtained by using $\text{Cs}_3\text{Cu}_2\text{I}_5$ and $\text{Cs}_3\text{Cu}_2\text{Cl}_5$ as phosphors.

1. INTRODUCTION

Metal-halide perovskite materials have attracted significant attention over the past decades owing to their advantages of high absorption coefficient, large carrier diffusion lengths, and superior photoelectric properties [1–4], which make them promising candidates for optoelectronic applications including solar cells [5–7], light-emitting diodes [8–14], photodetectors [15,16], and lasers [17–19]. Unfortunately, toxicity and poor stability are major obstacles that restrict their significant commercialization [20,21]. It is highly necessary to develop lead-free perovskite materials to solve these issues. So far, many efforts have been made to explore lead-free all-inorganic compounds through searching for low- or non-toxic elements to replace lead, including tin (Sn) [22–26], bismuth (Bi) [27–29], silver (Ag) [30,31], indium (In) [32,33], antimony (Sb) [34,35], germanium (Ge) [36,37], copper (Cu) [38–44], zinc (Zn) [45], magnesium (Mg) [46], and rare-earth ions [47]. Among these rising lead-free perovskite materials, cesium copper halide perovskites benefit from being low cost and earth abundant. In previous reports, a limited number of synthetic methods have been used to fabricate cesium copper halide perovskites, which depend on solvents with low recovery rates, causing a certain degree of environmental pollution [48]. Sustainable development of solvent-free technologies for the synthesis of cesium copper halide perovskites has become a critical issue.

The ball milling approach based on mechanochemistry, a kind of green and reemerging efficient synthetic method, was identified by the International Union of Pure and Applied Chemistry (IUPAC) as one of 10 world-changing technologies [49]. The process can promote physical and chemical reactions between solids quickly and quantitatively with no added solvent, consistent with sustainable development. Moreover, the ball milling method offers tremendous advantages compared to traditional solution-based methods by avoiding the solubility limitation for poorly soluble or insoluble reagents and achieving high yield in a relatively short time by controlling materials [50]. Recently, it has been adopted to fabricate lead halide perovskite materials [51,52]. However, there are no reports to our knowledge about using the ball milling approach to fabricate cesium copper halide perovskites. In this work, we first extended the ball milling method to prepare highly luminescent and stable $\text{Cs}_3\text{Cu}_2\text{I}_5$ and $\text{Cs}_3\text{Cu}_2\text{Cl}_5$ perovskite powders without solvent. The as-fabricated all-inorganic copper-based perovskites exhibit self-trapped excitons (STE) emission features including broad photolumines-
cent (PL) emission, large Stokes shift, long PL lifetime, and high PL quantum yield (QY) reaching 60%. The Cs3Cu2I5 and Cs3Cu2Cl5 perovskites with good thermal stability and photostability were employed as phosphors for UV-pumped phosphor-converted (pc)-LEDs.

2. EXPERIMENT

A. Materials and Synthesis
The materials used were cesium iodide (CsI, 99.9% metal basis, Aladdin), cuprous iodide (CuI, 99.9% metal basis, Aladdin), cesium chloride (CsCl, 99.5%, Macklin), and cuprous (I) chloride (CuCl, 99.5%, Macklin). All chemicals were used as received without further purifications. Cs3Cu2X5 powders were fabricated by the dry ball milling method at room temperature. In typical synthesis of Cs3Cu2I5 powder, 3 mmol CsI (0.779 g) and 2 mmol CuI (0.38 g) were first homogeneously mixed in a mortar; the mixture was then transferred into a grinding tank (steel bowl with steel ball, 10 mL). The sealed tank was mixed in a mortar; the mixture was then transferred into a grind- ing tank (steel bowl with steel ball, 10 mL). The sealed tank was mixed in a mortar; the mixture was then transferred into a grind- ing tank (steel bowl with steel ball, 10 mL). The sealed tank was mixed in a mortar; the mixture was then transferred into a grind-

B. Fabrication of UV-Pumped pc-LEDs
0.05 g of Cs3Cu2I5 powder and 0.05 g of Cs3Cu2Cl5 powder were mixed with a thermal-curable silicone resin OE-6551A (0.1 g) under vigorous stirring. The hardener OE-6551B (0.2 g) was added to form a fluorescent paste, and then the paste was deposited on a commercial GaN-based UV-LED chip (310 nm, EPILED Co., Ltd).

C. Characterization
The morphologies and elemental analysis of Cs3Cu2I5 and Cs3Cu2Cl5 powders were collected by scanning electron microscope (SEM), energy dispersive X-ray (EDX, FEI Quanta FEG 250 ESEM), and transmission electron microscope (TEM) (JEOL, JEM-2010F, 200 kV) equipped with an X-ray spectrometer detector. X-ray diffraction (XRD) patterns of Cs3Cu2I5 and Cs3Cu2Cl5 powders were recorded on an X-ray diffractometer (Bruker AXS D8) using Cu-Kα X-ray radiation (λ = 1.5406 Å). Thermogravimetric analysis (TGA) results of the powder were obtained using a PerkinElmer Diamond TG/DTA6300, conducted at a heating rate of 10°C·min⁻¹ to 1500°C in N2 flow with an alumina crucible. X-ray photoelectron spectroscopy (XPS) measurements were performed on a ULVAC-PHI instrument (PHIQUAN-TERA-II SXM) with Al Kα as the X-ray source at 70 W. The UV-Vis diffuse reflectance spectra of the powdered samples were taken on a PerkinElmer Lambda 35 double-beam spectrometer. PL and PL excitation (PLE) spectra were recorded on the Horiba PTI QuantaMaster 400. The absolute PL QY’s time-resolved PL decay curves were measured on an FLSP920 spectrophotofluorimeter (Edinburgh Instruments, TCSPC system) equipped with an integrating sphere.

D. Computational Methods
First-principle calculations of Cs3Cu2I5 were carried out using the Vienna Ab initio Simulation Package (VASP) code. To guarantee convergence, the projected augmented plane wave basis set was defined by a cutoff of 300 eV. The mesh samplings in the Brillouin zone (BZ) were 3 × 3 × 2. Experimental lattice parameters of Cs3Cu2I5 were used, and the atomic positions were fully relaxed until the residual forces were 0.05 eV Å⁻¹. Electronic band structures, density of states (DOS), and exciton properties were calculated using the hybrid PBE0 function.

3. RESULTS AND DISCUSSION
The schematic procedure of a typical fabrication of Cs3Cu2I5 powder by using a planetary ball mill is illustrated in Fig. 1(a): the raw powder materials of cesium iodide (CsI) and cuprous iodide (CuI) were first homogeneously mixed in a mortar; the mixture was then transferred into a steel bowl with a steel ball, and the blue emissive product was generated after a grinding process of the mixture for half an hour at room temperature, demonstrating an extremely energy-saving procedure compared to previous reports on lead perovskites [51–53]. The SEM image of the Cs3Cu2I5 powder is shown in Fig. 1(b), and it exhibits irregularly shaped particles with the diameter of 0.71 ± 0.3 μm, consistent with the TEM result [Fig. 1(c)]. The high-resolution TEM (HRTEM) image [Fig. 1(d)] of the Cs3Cu2I5 powder shows high crystallinity with a lattice fringe of 0.38 nm corresponding to the crystal plane (022). The high crystallinity feature also can be confirmed by the selected area electron diffraction (SAED) pattern as shown in the inset of Fig. 1(d). EDX measurement [Fig. 1(e)] was performed.
to estimate the chemical composition of Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} powder sample, which yielded a Cs:Cu:I ratio of ≈3:2:5, indicating that the Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} compound was successfully synthesized. Elemental mapping of the product has been performed to further confirm the presence of Cs, Cu, and I in the resulting Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} powder as shown in Figs. 1(f)–1(i), exhibiting the homogeneous distribution of three elements over the particles.

We performed XRD measurement to verify the phase structure of the as-synthesized Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5}; as shown in Fig. 2(a), the XRD patterns with main 2\theta positions of 13.1°, 15.1°, 23.9°, 25.6°, 26.3°, 28.2°, 30.6°, and 47.9° were assigned to the (111), (002), (122), (312), (222), (131), (313), and (152) planes of a bulk Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} (JCPDS No. 45-0077). These results indicate that the as-fabricated Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} powder has a orthorhombic crystal structure with a space group of \textit{Pnma}, consistent with previous reports [40]. The stability of Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} perovskite is a critical factor for its applications, and thus TGA was carried out to investigate the thermal stability of the Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} powder. Figure 2(b) shows that the as-synthesized Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} powder is stable to 560°C, indicating that it has a good thermal stability, the valence state and surface chemical composition of Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} powder as shown in Fig. 2(c), featuring a sharp absorption band centered at 324 nm. A bandgap value of 3.69 eV was given through the Tauc plot [inset of Fig. 2(c)].

The absolute PL QY of Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} was measured up to 60%, indicating that our sample has a strong emission feature. Figure 3(a) shows PL spectra of Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} powder under different excitation wavelengths ranging from 260 to 340 nm, with a uniform full width at half-maximum (FWHM) of 80 nm. Figure 3(b) predicts the PLE spectra of Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} with a fixed peak at 303 nm, which makes it suitable as phosphor for UV-pumped pc-LEDs. The large Stokes shift of 137 nm between the PLE and PL peaks illustrates that the emission mechanism cannot be explained simply by a direct band recombination emission [54,55]. UV-Vis optical diffuse reflectance spectroscopy was adopted to determine the optical bandgap of Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} powder as shown in Fig. 3(c), featuring a sharp absorption band centered at 324 nm. A bandgap value of 3.69 eV was given through the Tauc plot [inset of Fig. 3(c)]. To further explore excitonic recombination kinetics, the time-resolved PL decay curve of Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} powder was measured under 300 nm excitation as shown in Fig. 3(d). The PL decay can be described by monoexponential fitting, giving a long-lived PL lifetime of 1.13 μs that exhibits the phosphorescence feature of Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5}.

The thermal stability and photostability of perovskite materials are critical for their long-term application in lightings and displays. To evaluate the natural stability of Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} powder, the evolution of the PL spectra of Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} powder after thermal treatment under N\textsubscript{2} protection at different temperatures (100°C, 200°C, 300°C) was tested for half an hour. It can be seen clearly from Fig. 4(a) that the PL intensity of the Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} powder shows no decrease for 100°C and 200°C.
and only 21% reduction for 300°C compared to original value. Then the thermal stability of \( \text{Cs}_3\text{Cu}_2\text{I}_5 \) powder was tested at 100°C under ambient air environment. The emission intensity remained at 72% of the initial value after 5 h [Fig.4(b)], indicating that \( \text{Cs}_3\text{Cu}_2\text{I}_5 \) powder has a good thermal stability [57]. The photostability of \( \text{Cs}_3\text{Cu}_2\text{I}_5 \) powder was also studied [Fig. 4(c)] using a 500 W xenon lamp as the excitation source; the sample only exhibited a 22% reduction in PL intensity after 5 h illumination, which is better than Pb-based perovskites [58]. Interestingly, the \( \text{Cs}_3\text{Cu}_2\text{I}_5 \) powder had a remarkable stability in air; the XRD patterns of a \( \text{Cs}_3\text{Cu}_2\text{I}_5 \) powder exposed to ambient conditions for three months were identical to that of the initial as-synthesized powder [Fig. 4(d)]. PL intensity remained at 60% of the initial value after 90 days [Fig. 4(e)], much better than that of other reported perovskites [28,42,59]. The reason for the high stability of the as-fabricated \( \text{Cs}_3\text{Cu}_2\text{I}_5 \) perovskite is most likely that there are no organic species (organic ions and ligands) contained in its structure [60–62].

Notably, green emissive \( \text{Cs}_3\text{Cu}_2\text{Cl}_5 \) perovskite was achieved for the first time to our knowledge. The SEM image is shown in Fig. 5(a), and it exhibits irregularly shaped micrometer-sized particles of the obtained \( \text{Cs}_3\text{Cu}_2\text{Cl}_5 \). Figure 5(b) shows the HRTEM image of the \( \text{Cs}_3\text{Cu}_2\text{Cl}_5 \), indicating high crystallinity with a lattice fringe of 0.35 nm. The SAED pattern of the \( \text{Cs}_3\text{Cu}_2\text{Cl}_5 \) [inset of Fig.5(b)] further confirms the high crystallinity. EDX elemental mappings of the selected \( \text{Cs}_3\text{Cu}_2\text{Cl}_5 \) particles [Fig. 5(c)] showcase the uniform distribution of cesium, copper, and chlorine elements in the particles. The XRD pattern [Fig.5(d)] shows that the diffraction peak positions and corresponding intensities are mainly consistent with the bulk \( \text{Cs}_3\text{Cu}_2\text{Cl}_5 \) standard card (JCPDS No. 24-0247). The \( \text{Cs}_3\text{Cu}_2\text{Cl}_5 \) exhibits an orthorhombic phase structure with the lattice constants \( a = 9.176 \) Å, \( b = 10.505 \) Å, and \( c = 13.141 \) Å. We found that an additional \( \text{CsCl} \) phase signal appeared in the XRD pattern, which is marked with black stars; it is unavoidable for synthesis of chloride compounds [39,63]. The existing three elements were further confirmed by XPS results as shown in Fig. 5(e). The HRXPS analysis [Figs. 5(f) and 5(g)] of the Cs 3d (3d5/2, 724.2 eV; 3d3/2, 738.5 eV) and Cl 2p (198.3 eV) reveals that monovalent Cs\(^+\) and monovalent Cl\(^-\) existed in the \( \text{Cs}_3\text{Cu}_2\text{Cl}_5 \) sample [9,64], while the HRXPS spectrum of Cu 2p [Fig. 5(h)] provides two main peaks of monovalent Cu\(^+\) (932.6 eV, 953.2 eV) with two
of the TGA result [Fig. 5(i)], which shows that the product is stable to 500 °C, indicating that it displays a good thermal stability.

cause of the slight oxidation of partial photoluminescence originated from STEs [33,39]. Mott and Stoneham reported that the STE lifetime is related to the energy barrier that is required to be conquered for STE formation [66]. The potential barrier should be lower for Cs$_3$Cu$_2$I$_5$ compared to Cs$_3$Cu$_2$Cl$_5$, which may explain the shorter relaxation time for excitons in Cs$_3$Cu$_2$I$_5$ compared to that for excitons in Cs$_3$Cu$_2$Cl$_5$. It is consistent with the reported one [67]. The crystal structure of Cs$_3$Cu$_2$Cl$_5$ powder is similar to Cs$_3$Cu$_2$I$_5$ crystal, containing unique [Cu$_2$Cl$_3$]$_{3-}$ dimers made of a trigonal planar CuCl$_3$ sharing an edge with a tetrahedral CuCl$_4$ unit, all surrounded by Cs$^+$ [Fig. 6(d)]. And the electrons and phonons of Cs$_3$Cu$_2$Cl$_5$ are strongly coupled to induce Jahn–Teller distortion of polyhedron [Cu$_2$Cl$_3$]$_{3-}$ under UV light excitation. The excited-state electrons become self-trapped by the distortion and then release energy by a recombination process, and a similar emission behavior was also observed for other 0D lead-free crystal [68]. DFT calculations confirm that Cs$_3$Cu$_2$Cl$_5$ has a direct bandgap at the Γ point with the value of 2.45 eV [Fig. 6(e)]. Furthermore, the absolute PL QY of Cs$_3$Cu$_2$Cl$_5$ powder was measured up to 53%. The stability of the Cs$_3$Cu$_2$Cl$_5$ powder was also studied in air conditions at room temperature by detecting variations of XRD patterns and PL intensity for 60 days. The XRD patterns [Fig. 6(f)] of Cs$_3$Cu$_2$Cl$_5$ powder exhibit no changes; the PL intensity remained at 70% of the initial value, indicating that Cs$_3$Cu$_2$Cl$_5$ powder also has better stability than other reported perovskites [28,42,59].

In order to illustrate the potential lighting application of the obtained perovskite powders, we fabricated a UV-pumped pc-LED device by using blue emissive Cs$_3$Cu$_2$I$_5$ and green emissive Cs$_3$Cu$_2$Cl$_5$ as phosphors. It is the first time to our knowledge that pc-LED based on all copper-based perovskites without other phosphors has been prepared. Figure 7(a) provides a photograph of the as-fabricated pc-LED with brown
The authors declare no conflicts of interest.

In summary, we have developed a simple and energy-saving route to synthesize stable lead-free perovskites in a dry ball milling process. The obtained blue emissive Cs₃Cu₂I₅ powder exhibits a high PL QY of 60% with a long lifetime of 1.13 μs and a huge Stokes shift of 137 nm. The luminescence mechanism of Cs₃Cu₂I₅ could be explained by self-trapped excitons that originate from Jahn–Teller distortion of the Cu tetrahedral site. The green emissive Cs₃Cu₂Cl₅ perovskite with PL QY of 53% was successfully fabricated by using the same process for the first time, with the PL peak at 510 nm. We finally realized a UV-pumped LED device by using blue emissive Cs₃Cu₂I₅ and green emissive Cs₃Cu₂Cl₅ as phosphors.

**Funding.** National Key R&D Program of China (2017YFB1002900); National Natural Science Foundation of China (51602024, 61420106014, 61574017, 61775019); Beijing Nova Program (Z17110001117047); Beijing Outstanding Young Scientist Program (BJJWZYJH01201910007022); Opened Fund of the State Key Laboratory on Integrated Optoelectronics (IOSKL2017KF13).

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

This work was supported by the National Natural Science Foundation of China (51671088) and the National Key Research and Development Program of China (2017YFA0204601). The authors declare no conflicts of interest.

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