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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 photovoltaic 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 Cs$_3$Cu$_2$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 Cs$_3$Cu$_2$I$_5$ and green emissive Cs$_3$Cu$_2$Cl$_5$ lead-free perovskite powders have good thermal stability and photostability. Furthermore, UV-pumped phosphor-converted light-emitting diodes were obtained by using Cs$_3$Cu$_2$I$_5$ and Cs$_3$Cu$_2$Cl$_5$ as phosphors. © 2020 Chinese Laser Press

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 Cs$_3$Cu$_2$I$_5$ and Cs$_3$Cu$_2$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 Cs₃Cu₃Cl₅ 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 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 a 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 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. Electronic band structures, density of states (DOS), and exciton properties were calculated using the hybrid PBE0 function.

B. Fabrication of UV-Pumped pc-LEDs

0.05 g of Cs₃Cu₂I₅ powder and 0.05 g of Cs₃Cu₃Cl₅ powder were mixed with a thermal-curable silicone resin OE-6551A (0.779 g) and 2 mmol CuI (0.38 g) were first homogeneously mixed in a mortar; then 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].

C. Characterization

The morphologies and elemental analysis of Cs₃Cu₂I₅ and Cs₃Cu₃Cl₅ 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 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 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 a 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 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. Electronic band structures, density of states (DOS), and exciton properties were calculated using the hybrid PBE0 function.

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

![Fig. 1.](image-url)
to estimate the chemical composition of Cs$_3$Cu$_2$I$_5$ powder sample, which yielded a Cs:Cu:I ratio of $\approx$3:2:5, indicating that the Cs$_3$Cu$_2$I$_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$_3$Cu$_2$I$_5$ 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$_3$Cu$_2$I$_5$: 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$_3$Cu$_2$I$_5$ (JCPDS No. 45-0077). These results indicate that the as-fabricated Cs$_3$Cu$_2$I$_5$ powder has a orthorhombic crystal structure with a space group of Pnma, consistent with previous reports [40]. The stability of Cs$_3$Cu$_2$I$_5$ perovskite is a critical factor for its applications, and thus TGA was carried out to investigate the thermal stability of the Cs$_3$Cu$_2$I$_5$ powder. Figure 2(b) shows that the as-synthesized Cs$_3$Cu$_2$I$_5$ powder is stable to 560°C, indicating that it has a good thermal stability, which is critical for its applications, and thus TGA was carried out to estimate the thermal stability of the Cs$_3$Cu$_2$I$_5$ compound. Figure 3(b) shows that the as-synthesized Cs$_3$Cu$_2$I$_5$ sample, which yielded a Cs:Cu:I ratio of 3:2:5, indicating that our sample has a strong emission feature. Figure 3(a) shows PL spectra of Cs$_3$Cu$_2$I$_5$ 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$_3$Cu$_2$I$_5$ 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 spectrosopy was adopted to determine the optical bandgap of Cs$_3$Cu$_2$I$_5$ 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$_3$Cu$_2$I$_5$ 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$_3$Cu$_2$I$_5$. Summarizing the optical features of the Cs$_3$Cu$_2$I$_5$ sample, including a broad PL spectrum, a large Stokes shift, and a long PL decay time, we can deduce that the emission of Cs$_3$Cu$_2$I$_5$ is ascribed to the STE recombination mechanism due to the Jahn–Teller distortion of the polyhedron (formed by Cu$^+$ and I$^-$) in the excited states [33,56]. The electronic structure calculations were performed using density functional theory (DFT) to further study the fluorescence mechanism of the Cs$_3$Cu$_2$I$_5$ powder, first giving the crystal structure of the Cs$_3$Cu$_2$I$_5$ as viewed down the a axis [Fig. 3(e)] consisting of caged [Cu$_2$I$_3$]$^-$ units with tetrahedral and trigonal Cu$^+$ sites, isolated by Cs$^+$ ions. Figure 3(f) provides the density of states (DOS) of the Cs$_3$Cu$_2$I$_5$ sample, indicating that the valence band maximum (VBM) is mainly composed of Cu 3d orbits, while the conduction band maximum (CBM) originates from Cu 4s and I 5p orbits, and Cs$^+$ has no contribution to CBM or VBM [40]. This means that the [Cu$_2$I$_3$]$^-$ polyhedron plays the dominant role in the crystal distortion and emission mechanism of Cs$_3$Cu$_2$I$_5$, which can confine the excitons trapped by Jahn–Teller distortion in excited states. This is consistent with the previous reports [40,54]. Additionally, DFT calculations also yielded that Cs$_3$Cu$_2$I$_5$ crystal has a direct bandgap at the $\Gamma$ point with the gap value of 3.70 eV [Fig. 3(g)]. The excitation and emission processes for Cs$_3$Cu$_2$I$_5$ are described in Fig. 3(h): after excitation with a high-energy ultraviolet light, the electron moves first from the ground states to the excited states, and then transits from singlet to triplet states (self-trapped states). Subsequent transition of the electron from the STE states to the ground states occurs, accompanied by blue emission.

The thermal stability and photo-stability of perovskite materials are critical for their long-term application in lightings and displays. To evaluate the natural stability of Cs$_3$Cu$_2$I$_5$ powder, the evolution of the PL spectra of Cs$_3$Cu$_2$I$_5$ powder after thermal treatment under N$_2$ 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$_3$Cu$_2$I$_5$ powder shows no decrease for 100°C and 200°C.
and only 21% reduction for 300°C compared to original value. The thermal stability of Cs₃Cu₂I₅ 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 Cs₃Cu₂I₅ powder has a good thermal stability [57]. The photostability of Cs₃Cu₂I₅ 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 Cs₃Cu₂I₅ powder had a remarkable stability in air; the XRD patterns of a Cs₃Cu₂I₅ 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 Cs₃Cu₂I₅ perovskite is most likely that there are no organic species (organic ions and ligands) contained in its structure [60–62].

Notably, green emissive Cs₃Cu₂Cl₅ 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 Cs₃Cu₂Cl₅. Figure 5(b) shows the HRTEM image of the Cs₃Cu₂Cl₅, indicating high crystallinity with a lattice fringe of 0.35 nm. The SAED pattern of the Cs₃Cu₂Cl₅ [inset of Fig. 5(b)] further confirms the high crystallinity. EDX elemental mappings of the selected Cs₃Cu₂Cl₅ 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 Cs₃Cu₂Cl₅ standard card (JCPDS No. 24-0247). The Cs₃Cu₂Cl₅ 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 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; 3d⁷/₂, 738.5 eV) and Cl 2p (198.3 eV) reveals that monovalent Cs⁺ and monovalent Cl⁻ existed in the Cs₃Cu₂Cl₅ 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.

The excited-state electrons become self-trapped by the distortion of polyhedron [Fig. 6(d)]. And the electrons and phonons are strongly coupled to induce Jahn–Teller distortion of polyhedron [Cs2CuCl6]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 Cs3Cu2I5 has a direct bandgap at the Γ point with the value of 2.45 eV [Fig. 6(e)]. Furthermore, the absolute PL QY of Cs3Cu2Cl5 powder was measured up to 53%. The stability of the Cs3Cu2Cl5 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 Cs3Cu2Cl5 powder exhibit no changes; the PL intensity remained at 70% of the initial value, indicating that Cs3Cu2Cl5 powder 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 Cs3Cu2I5 and green emissive Cs3Cu2Cl5 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
Fig. 7. (a) Photograph of the as-fabricated pc-LED based on dual phosphors of blue emissive Cs3Cu2I5 and green emissive Cs3Cu2Cl5. (b) Photograph of the pc-LED device operated at a forward bias current of 20 mA. (c) EL spectrum and (d) CIE chromaticity diagram of the LED device.

The authors declare no conflicts of interest.

Disclosures. The authors declare no conflicts of interest.

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