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One-step solution synthesis of white-light-emitting films via dimensionality control of the Cs–Cu–I system

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ABSTRACT
Low-dimensional lead-free luminescent halides have emerged as highly promising phosphors for white-light emission. Recently, we reported a broadband blue-emitting copper(I) iodide-based material, Cs₃Cu₂I₅, with a high photoluminescence quantum yield (PLQY) (∼90%) and a zero-dimensional nature, providing significant dimensionality for the photoactive site. However, this material is insufficient as a white-light emitter owing to the deficient yellow emission. In this paper, we report a novel yellow luminescent phosphor, CsCu₂I₃, with a 1D structure for the photoactive site. This material exhibits a broadband emission centered at ∼560 nm with a PLQY of ∼8%. We demonstrate a thin film with white-light emission that can be fabricated using one-step spin-coating of a mixed precursor solution of 1D CsCu₂I₃ (yellow) and 0D Cs₃Cu₂I₅ (blue).

INTRODUCTION
The discovery of new solid-state lighting (SSL) holds great potential for a variety of applications, such as white-light-emitting diodes (LEDs), smart windows, and photodetectors. Among the applications of SSL, white LEDs have steadily emerged as a replacement for the conventional incandescent and fluorescent lamps in our life because of their low-energy consumption and high efficiency. Typical white LED devices consist of a blue LED (InGaN chip) coated with yellow inorganic phosphor. Inorganic phosphors are generally composed of a single phase of a host matrix doped with a rare earth ion, such as Eu²⁺ and Ce³⁺. Despite the considerable advances of white LEDs, the supply risk for these rare earth materials and the high cost are still problems. Conventional quantum dot (QD)-based down-conversion phosphors are a potential candidate for this application. However, this class of materials is also limited for use in white LEDs owing to the toxicity of including chemical elements, such as Cd and Pb, and their complicated synthesis process. Although lead halide-based perovskites, such as CaPbX₃, have drawn wide interest for their remarkable optical properties and facile synthesis, their performance for white LED applications is now limited for several reasons. The first issue is the low photoluminescence quantum yield (PLQY) due to the easy dissociation of excitons. The second is the relatively poor coverage of their luminescent spectra because of the narrow full width at half maximum (FWHM < 25 nm). In addition, this material suffers from reabsorption losses originating from a small Stokes shift. Therefore, developing eco-friendly broadband emission materials with a large Stokes shift and a high PLQY is an effective approach for resolving these issues.

Control of dimensionality in photoactive sites is a way to achieve broadband emission, a large Stokes shift, and a high PLQY. Low-dimensional metal halide-based materials, such as corrugated 2D, 1D, and 0D materials, have attracted attention as a new class of functional materials with unique optoelectronic properties that are significantly different from those of 3D materials.
Generally, the luminescence of these 3D materials originates from the direct transition associated with a low exciton binding energy, leading to a small Stokes shift, narrow FWHM, and low PLQY. Unlike typical 3D materials, broadband emission, a large Stokes shift, and a high PLQY have been observed in low-dimensional materials owing to self-trapped exciton formation or excited state structural reorganization, which is commonly observed in halide-based semiconductors. Consequently, low-dimensional halide materials provide an opportunity for the presence of an emitting layer based semiconductors. In particular, the 1D CsCu$_2$I$_5$ may be regarded as having a 0D bulk core/shell structure, and it provides a broadband blue emission (∼445 nm) and large Stokes shift (∼245 nm) and has a PLQY of ∼8%. We succeeded in fabricating a white luminescent thin film by a one-step spin-coating method using a mixed precursor solution of 1D CsCu$_2$I$_5$ (yellow) and 0D Cs$_3$Cu$_2$I$_5$ (blue) to achieve full coverage in the visible range of the spectrum. This will provide distinct merits for its practical application.

Figure 1(a) shows the crystal structure of γ-Cul, which consists of a 3D network of CuI tetrahedra. Each layer of CuI tetrahedra is connected to each other by sharing corners (3D Cul). As shown in Fig. 1(b), 3D Cul has a direct bandgap at the Γ point. The conduction band minimum (CBM) and the valence band maximum (VBM) result from Cu 4s + I 5p and Cu 3d + I 5p, respectively. In contrast, Fig. 1(c) shows the crystal structure of 1D CsCu$_2$I$_5$ (unit cell: $a = 10.5479$ Å, $b = 13.1752$ Å, $c = 6.09718$ Å, and $α = β = γ = 90°$), which belongs to the orthorhombic space group of $Cmcm$. This crystal has a chain of CuI tetrahedrons, and Cs cations occupy the cavity position, which is surrounded by Γ. 1D Cul has a direct bandgap at the Γ point [see Fig. 1(d)]. As shown in Fig. 1(e), the PDOS indicates that the VBM is composed mainly of Cu 4s orbitals and I 5p orbitals, and the CBM is derived from Cs 5s and I 5p orbitals. Cs$^+$ does not contribute to the CBM or VBM but contributes to the widening of the bandgap. 1D CsCu$_2$I$_5$ has a regular bulk assembly of 1D core-shell wire structures. Notably, as shown in Figs. 1(b) and 1(d), the valence and conduction bands of Cul are more dispersive than those of CsCu$_2$I$_5$, indicating that the electron and hole effective masses ($m_e^*$ and $m_h^*$, respectively) are smaller than those for 1D CsCu$_2$I$_5$ (see Table S1).
To demonstrate the optical properties of 1D CsCu$_2$I$_3$, a simple wet chemical method involving inverse temperature solubility behavior in specific solvents was used to synthesize the 1D CsCu$_2$I$_3$ single crystals. The resulting single crystals of 1D CsCu$_2$I$_3$ (Fig. 2(a)) were shown to have an orthorhombic space group of Cmcm, as confirmed by single crystal X-ray diffraction (Fig. S1). The results of the chemical composition analysis on various samples using an electron probe microanalyzer (EPMA; Table S2) indicated that the composition was homogeneous and agreed with Cs:Cu:I = 1:2:3.

The TEM image substantiated the lattice image and agrees with the structure of 1D CsCu$_2$I$_3$, as shown in Fig. 2(b). The photoluminescence (PL) peak wavelength is located at $\sim$560 nm with a broad FWHM ($\sim$107 nm). The PLQY of $\sim$8% was obtained at room temperature.

Figure 2(c) shows the temperature dependence of the PL. The exciton binding energy was determined using the following equation:

$$I(T) = \frac{I_0}{1 + A \exp \left( \frac{E_b}{k_B T} \right)},$$  \hspace{1cm} (1)

where $I(T)$ is the PL intensity at temperature $T$, while $I_0$ is the PL intensity at the low temperature limit, $E_b$ is the exciton binding energy, and $k_B$ is the Boltzmann constant. The exciton binding energy was determined to be $\sim$315 meV, which is much higher than that of 3D CuI ($\sim$62 meV). One plausible explanation is that the exciton generated in 1D CsCu$_2$I$_3$ is confined within the CuI$_4$ tetrahedral chain. A tightly bound exciton is difficult to dissociate, resulting in the high PLQY of 1D CsCu$_2$I$_3$. The exciton lifetime estimated from Fig. 2(d) of 1D CsCu$_2$I$_3$ was $\sim$149 ns at room temperature, which is similar to other low-dimensional materials involving excited state structural reorganization.

To attain more optical properties, the 1D CsCu$_2$I$_3$ thin film was also fabricated on a glass substrate via the spin-coating method. The results of the chemical composition analysis by EPMA and glancing angle XRD indicated that the 1D CsCu$_2$I$_3$ thin film was successfully fabricated (Fig. S2 and Table S3). Both the single crystal and the thin film exhibited the same PL characteristics (Fig. S3). The photoluminescence excitation (PLE) and PL peak wavelengths were 315 and 560 nm, respectively, as shown in Fig. 2(e). A large Stokes shift of $\sim$245 nm and only one emission peak position.
It is thus plausible that the excited state structural reorganization dominates the PL mechanism of 1D CsCu$_2$I$_3$. The excited state structural reorganization is explained well by the Jahn–Teller distortion of the CuI$_4$ tetrahedral site in the excitation state.$^{23,30,31}$

Figure 3(a) shows a photograph of 1D CsCu$_2$I$_3$ and 3D CuI upon UV excitation. 3D CuI exhibits weak violet emission, whereas 1D CsCu$_2$I$_3$ exhibits bright yellow emission. Table I summarizes the optical properties of the copper(i) iodide-based compounds with different dimensionalities of the photoactive site (CuI$_4$). First, the low-dimensional copper(i) iodide-based compounds exhibited broadband emission, relatively large Stokes shift, and long lifetime. The excitation and recombination processes for these compounds can be described by the schematic configuration coordinate diagram shown in Fig. 3(b). The materials in which excitons are tightly confined have a high exciton binding energy and a high PLQY. However, as shown in Fig. 5(b), the absorption and emission spectra of 3D CuI have peaks at 400 and 425 nm, respectively. The exciton is easily dissociated into free carriers, and the resulting carriers diffuse at the CBM and VBM. In this case, luminescence occurs near the band edge via the direct recombination of mobile holes and electrons. Thus, 3D CuI has a low PLQY with a narrow FWHM, small Stokes shift, and short lifetime [see Fig. 3(c)]. This correlation suggests that the optical properties of this system primarily originate from their dimensionality of photoactive sites in the crystal structure.

The application of this 1D CsCu$_2$I$_3$ as a broadband white luminescent thin film was investigated using the one-step spin-coating method with the blue-emitting 0D Cs$_3$Cu$_2$I$_5$ phosphor. These materials have exceptional properties: broadband emission and no self-absorption. Each of these materials has a high solubility in the same solvent, such as dimethylsulfoxide (DMSO) or dimethylformamide (DMF). Thus, we fabricated the white luminescent thin films by using a solution process. First, 1D CsCu$_2$I$_3$ and 0D Cs$_3$Cu$_2$I$_5$ solutions were admixed at different molar ratios. Then, the mixed solutions were spin-coated on bare glass. The thin films fabricated by the one-step spin-coating method exhibited white luminescence under UV illumination, as shown in Fig. 4(a). The broadband spectrum shows that the two components of 1D CsCu$_2$I$_3$ (~560 nm) and 0D Cs$_3$Cu$_2$I$_5$ (~445 nm) are both present [see Fig. 4(b)]. The broadband white luminescence covers the mostly full visible spectrum. The spectrum for the 83:17 sample was located on Commission Internationale de l’Eclairage (CIE) coordinates of (0.33, 0.35), as shown in Fig. 4(c).

We found a novel yellow luminescent material, CsCu$_2$I$_3$, that has a 1D structure with photoactive sites. The material exhibits a broadband emission (~107 nm) with a relative Stokes shift of 245 nm and a PLQY of ~8%. A comparison of the PL properties was made between CuI(3D), CsCu$_2$I$_3$(1D), and Cs$_3$Cu$_2$I$_5$(0D) for different structural dimensionalities of the photoactive site. White emission thin films were fabricated by one-step spin-coating method with an admixed solution precursor of 1D CsCu$_2$I$_3$ (yellow) and 0D Cs$_3$Cu$_2$I$_5$ (blue), both of which were soluble in the same solvent.

**TABLE I.** Comparison of the optical properties of the copper(i) iodide-based compounds with different dimensionalities.

| Chemical formula | Dimension | Excitation/ Emission (nm) | FWHM (nm) | Stokes shift (nm) | PLQY (%) | Exciton binding energy (meV) | Lifetime (ns) | Reference |
|------------------|-----------|---------------------------|-----------|------------------|----------|----------------------------|--------------|----------|
| Cs$_3$Cu$_2$I$_5$ | 0D        | 290/445                  | ~80       | ~155             | ~90      | ~490                      | ~464         | 23       |
| CsCu$_2$I$_3$    | 1D        | 315/560                  | ~107      | ~245             | ~8       | ~315                      | ~149         | This work |
| CuI              | 3D        | 400/425                  | ~14       | ~25              | <0.01    | 62                        | <0.7         | 29       |

The CIE 1913 color space was used to represent the color of the thin films. The CIE 1913 chromaticity coordinates for the 83:17 sample are (0.33, 0.35), as shown in Fig. 4(c).

**FIG. 4.** (a) Photograph of the thin films of 1D CsCu$_2$I$_3$, 0D Cs$_3$Cu$_2$I$_5$, and its mixtures (from left to right: CsCu$_2$I$_3$, the one-step synthesized thin film with a mixture of 83(CsCu$_2$I$_3$):17(Cs$_3$Cu$_2$I$_5$), and Cs$_3$Cu$_2$I$_5$ under UV illumination. (b) PL spectrum of the mixture of 1D CsCu$_2$I$_3$ and 0D Cs$_3$Cu$_2$I$_5$ at different molar ratios. (c) CIE coordinates of PL from the thin film mixtures.
EXPERIMENTAL

Materials

Cesium iodide (CsI, 99.9%), copper(I) iodide (CuI, 99.999%), dimethylformamide (DMF, 99.8%), and dimethylsulfoxide (DMSO, ≥99.5%) were purchased from Sigma-Aldrich. Toluene was purchased from Wako. The precursors and solvent were used without further purification.

Single crystal growth of CsCu$_2$I$_3$ using the inverse temperature crystallization (ITC)

The CaI–CuI (CaI:CuI molar ratio of 1:2) solution was prepared using DMF as the ITC solvent. The solution concentration was 0.25M. The precursor solution was stirred at room temperature. Subsequently, the solution was titrated using toluene. This saturated solution was filtered using PTFE 0.45-μm pore size syringe filters. The filtered solution was injected in a vial, and the vial was kept on a hotplate at 100 °C for 30 min to allow the single crystal to grow. Thereafter, a CsCu$_2$I$_3$ single crystal with a size of ~2 mm was obtained.

Fabrication of the CsCu$_2$I$_3$ thin film and one-step spin-coating method

A 1M solution of CsCu$_2$I$_3$ precursors was prepared at ambient conditions while stirring for 4 h until no powder was observed in the DMSO and DMF that were used as the mixed solvent. Then, the thin film was formed by spin-coating the filtered solutions at 3000 rpm for 60 s on a glass substrate. The resulting thin film was annealed at 120 °C for 10 min. For the fabrication of the white luminescent thin film via the one-step coating method, 1M CsCu$_2$I$_3$ and 0.05M Cs$_3$Cu$_3$I$_7$ solutions were prepared. Then, these precursor solutions were mixed at different mixing ratios. Subsequently, one-step spin-coating was performed at 3000 rpm for 60s on a glass substrate. The resulting thin film was heated at 120 °C for 10 min.

Characterization methods

Single crystal XRD data were collected using a four-axis diffractometer (Rigaku: R-AXIS RAPID II, Mo Kα radiation), where the crystal was mounted on a glass capillary. The unit cell refinement was performed using software (Rigaku: Crystal Clear). The atomic arrangement of the single crystal was investigated using a transmission electron microscope (JEOL: JEM-2010F). The composition was obtained using a scanning electron microscope [SEM-EPMA; JEOL: JSM-7600F]. The thin film structures were examined by XRD (XRD) using a 2θ/θ scanner (Rigaku ATX-G, rotating Cu target source). The standard PL spectrum was obtained using fluorescence spectrophotometer (Hitachi: F-4500). The temperature dependence and decay profiles for the PL spectra were measured under the excitation of 300-nm light generated by the frequency doubling of 600-nm light obtained from a femtosecond laser system (Light Conversion: Pharos) and an optical parametric amplifier (Light Conversion: Orpheus). The temperature dependent PL spectrum was recorded using a spectrometer (Ocean Optics: USB2000+), where the sample temperature was controlled by a liquid He flow and a heater. PL decay curves were recorded using a streak camera equipped with a monochromator (Hamamatsu Photonics: C4334). The PLQY data were acquired using a quantum yield measurement system (Hamamatsu Photonics: C10027-01).

DFT calculations

First-principles calculations for 1D CsCu$_2$I$_3$ were carried out using a VASP code. The crystal structures (internal forces and external pressure) were optimized using the exchange correlation functional of Perdew, Burke, and Ernzerhof that was revised for solids. To ensure convergence, the projected augmented plane wave basis set was defined by a cutoff of 400 eV. The mesh samplings in the Brillouin zone were 4 × 4 × 3.

SUPPLEMENTARY MATERIAL

See the supplementary material for calculated effective masses with different dimensions for copper(I) iodide-based materials, single crystal XRD, EPMA of single crystal of CsCu$_2$I$_3$, thin film XRD and EPMA of thin film of CsCu$_2$I$_3$, photoluminescence spectra of the thin film and single crystal of 1D CsCu$_2$I$_3$, and UV–vis absorption and PL spectra of the thin films of 1D CsCu$_2$I$_3$ and 3D CuI.

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