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Letter

Blue-Violet Emission with Near-Unity Photoluminescence Quantum Yield from Cu(I)-Doped Rb₃InCl₆ Single Crystals

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their unique optoelectronic properties. In this study, we report a solid-state synthesis of airstable all-inorganic Pb-free zero-dimensional (0D) Rb₃InCl₆ single crystals (SCs). By a heterovalent doping of Cu⁺ ions, the Rb₃InCl₆:Cu⁺ SCs featured an efficient blue-violet emission with a greatly enhanced photoluminescence (PL) quantum yield (95%) and an ultralong PL lifetime (13.95 μ s). Combined with temperature-dependent PL and density functional theory calculations, we conclude that the efficient electronic isolation, enhanced exciton—phonon coupling, and electronic structure modulation after doping lead to bright blue-violet emission. Furthermore, the SCs exhibited excellent stability, maintaining 90% of the initial PL intensity after being stored in ambient conditions for more than two months. The results provide a new strategy for improving the optoelectronic properties of 0D allinorganic metal halides, which is promising for potential light-emitting applications.



Recently, halide perovskite has captured widespread research attention because of its outstanding performance in optoelectronic applications, such as solar cells,^{1,2} lightemitting diodes (LEDs),^{3–5} and optical pumping lasers.^{6,7} However, the issues of Pb toxicity, poor stability, and low lightemitting quantum efficiency have severely hindered the practical applications of this perovskite. Zero-dimensional (0D) Pb-free metal halides have the advantages of highly tunable structures and excellent stability. Furthermore, no potential energy barrier exists between free excitons and strongly localized excited states, creating favorable conditions for the formation of self-trapped excitons (STEs).⁸ 0D metal halides typically exhibit a broadband photoluminescence (PL) emission with a large Stokes shift due to a strong structural deformation, avoiding self-absorption in efficient white-light emitters.^{9,10}

Although highly emissive 0D metal halides consisting of tetrahedron BX_{4} , pyramid BX_{5} , and octahedron BX_{6} (where B refers to metal, and X refers to halogen) have been reported successively, most of them are yellow, ^{11,12} red, ¹³ or green¹⁴ emitters with a low PL quantum yield (PLQY). By contrast, 0D single crystals (SCs) as blue-violet light sources with a high PLQY are rarely reported.¹⁵ This largely results from the significant Stokes shift of 0D materials.¹⁶ Consequently, the development of Pb-free blue-violet emitters to cover the entire visible region is of great importance.

Elemental doping is considered an excellent strategy to expand the luminescence properties and improve the PLQY of 0D metal halides.¹⁷ This is because, compared with threedimensional halide perovskites, the isolated metal halide polyhedral units in 0D structures avoid the interaction between the polyhedra.¹⁸ Therefore, each isolated polyhedral unit in this particular host–guest system greatly determines the properties of the 0D metal halides.¹⁴ As a result, a partial replacement of the metal elements in the center of the polyhedra can considerably change the properties of the 0D materials. By exploiting the solution cooling method, Tan et al.¹⁹ realized a dark-blue emission in Cs₂SnCl₆ by introducing Bi³⁺ and an increased PLQY of ~80%. Recently, Han et al.²⁰ and Majher et al.²¹ raised the PLQY of Rb₃InCl₆ from less than 2% to more than 90% by Sb³⁺ substitution. Obviously, doping significantly increases the luminous efficiency of 0D metal halides.

In this work, we prepared pure-phase Pb-free 0D Rb₃InCl₆ SCs by a solid-state reaction method. Compared with the previous synthesis of Rb₃InCl₆ SCs through a hydrate Rb₂InCl₅·H₂O intermediate via a two-step solution process,^{20,21} the employed preparation process has the advantages of a direct synthesis and significantly simplified procedures.^{22,23} The pristine Rb₃InCl₆ shows a weak blue emission with a PL peak at 434 nm, similar to previous results. Furthermore, the heterovalent doping of Cu⁺ was used here to improve the luminous performance of the host Rb₃InCl₆ SCs. After it was

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doped, the $Rb_3InCl_6:Cu^+$ exhibited a strong blue-violet emission with the PL peak position shifted to 398 nm and the PLQY increased to 95%. Temperature-dependent PL measurements and density functional theory (DFT) calculations were performed to understand the underlying emission mechanisms.

Transparent bulk Rb₃InCl₆ SCs were grown by a spontaneous bulk crystallization via a slow cooling of the melts of a well-ground stoichiometric mixture of RbCl and InCl₃ at 750 °C in vacuumed and sealed 9 mm diameter quartz tubes. The specific growth parameters are described in the Supporting Information. The crystal structure was determined by single-crystal X-ray diffraction (SCXRD), which displayed a monoclinic structure with the C2/c space group with cell parameters of a = 25.27 Å, b = 7.73 Å, c = 12.41 Å, and $\beta = 99.618^{\circ}$. The refinement details and the crystallographic information file are included in the Supporting Information (Tables S1 and S2). As presented in Figure 1a, the asymmetric



Figure 1. (a) Simplified crystal structure of Rb_3InCl_6 . (b) The PXRD patterns of pure-phase Rb_3InCl_6 SCs and that doped with Cu⁺ and Cu²⁺ ions. The simulated PXRD pattern of Rb_3InCl_6 from the SCXRD result was also shown. (c) Magnified view of the (111) peak.

unit in the crystal structure consists of isolated $[InCl_6]^{3-}$ octahedral units and Rb⁺ cations. Each $[InCl_6]^{3-}$ octahedra is composed of a unique In site with a +3 oxidation state coordinated with six Cl⁻ ions, which is spatially isolated by surrounding Rb⁺ ions. The distance between two adjacent In³⁺ of Rb₃InCl₆ is ~7.47–7.73 Å, indicating that there is almost no chemical bonding between two adjacent $[InCl_6]^{3-}$ octahedra and that this crystal has a 0D electronic dimensionality. The powder X-ray diffraction (PXRD) pattern of Rb₃InCl₆ SCs matched well with the calculated result (Figure 1b), proving that the Rb₃InCl₆ SCs obtained from a solid-state synthesis were of high purity.

 Rb_3InCl_6 SCs prepared via the solid-state method performed a low PLQY of 8%.²⁰ To enhance the luminous performance, copper (Cu⁺ and Cu²⁺) ions were incorporated into the crystal structure. The PXRD patterns of Rb₃InCl₆, Rb₃InCl₆:Cu⁺ (doped with 5% Cu⁺), and Rb₃InCl₆:Cu²⁺ (doped with 5% Cu²⁺) are demonstrated in Figure 1b. Intriguingly, the two doped samples had almost identical PXRD patterns, indicating that Cu⁺ and Cu²⁺ doping resulted in the same crystal structure. Furthermore, the diffraction peaks of doped samples exhibited a slight peak shift to lower angles compared with pristine Rb₃InCl₆ (Figure 1c), suggesting that Cu doping caused the lattice expansion in the SCs. The energy-dispersive X-ray spectroscopy (EDS) elemental mapping results indicate that Rb, In, Cl, and Cu elements were uniformly distributed in the doped SCs (Figure S1).

The photophysical properties of Rb₃InCl₆ and $Rb_3InCl_6:Cu^+/Cu^{2+}$ SCs were comprehensively explored. The optical absorption spectra were generated from the diffuse reflection data by Kubelka–Munk function: $\alpha = (1 - R)^2/2R$, where α is the absorption coefficient, and *R* is the reflectance. As presented in Figure 2a, Rb₃InCl₆ had a sharp absorption edge at 230 nm along with a weak band tail ranging from 240 to 350 nm, corresponding to the singlet and triplet energy states, respectively.²⁴ The absorption characteristics were similar to that of the previously reported Cs2AgInCl6 double perovskite with two absorption peaks.^{21,25} The absorption spectra of the two doped samples exhibited similar band features, consistent with the PXRD results. Furthermore, compared with pristine Rb₃InCl₆, the strong absorption bands of doped samples remained almost unchanged, whereas the weak absorption peak was red-shifted to 306 nm.²⁰ From the Tauc plots (Figure 2b), band gaps of 5.43 and 5.29 eV were obtained for pristine Rb₃InCl₆ and Rb₃InCl₆:Cu⁺/Cu²⁺, respectively. These large band gap values were attributed to the large spacing of $[InCl_6]^{3-}$ octahedra with the 0D electronic structure.

From the above discussions, the PXRD patterns and absorption spectra of the $Rb_3InCl_6:Cu^+/Cu^{2+}$ by doping Cu in two valence states in the solid-state reaction were the same. On the basis of formula 1, we assume that it was due to the conversion of Cu^{2+} to Cu^+ at a high temperature during the solid-state synthesis.

$$2\mathrm{CuCl}_2 = 2\mathrm{CuCl} + \mathrm{Cl}_2 \uparrow \tag{1}$$

To verify this assumption, an X-ray photoelectron spectroscopy (XPS) measurement was performed (Figure 2c,d). The Cu⁺-doped SC showed two obvious peaks at the binding energies of 932.7 eV (Cu $2p_{3/2}$) and 952.6 eV (Cu $2p_{1/2}$), which agreed with the data of previous reports.^{26,27} For the Cu²⁺-doped sample, both Cu²⁺ and Cu⁺ signals were observed. Remarkably, the Cu⁺ peaks at 932.5 eV (Cu 2p_{3/2}) and 952.3 eV (Cu $2p_{1/2}$) were much stronger than the Cu²⁺ peaks at 934.8 eV (Cu $2p_{3/2}$) and 954.6 eV (Cu $2p_{1/2}$), indicating that most of the Cu²⁺ was reduced to Cu⁺ during the solid-state synthesis process. To further prove the conversion of Cu^{2+} to Cu⁺, we calculated the decomposition enthalpy (ΔH_d) of CuCl₂ by DFT with a value of 2.88 meV/atom, which indicates that Cu²⁺ can be converted to Cu⁺ under a high-temperature reaction. In addition, we observed small pores on the surface of the SCs doped with Cu²⁺ (Figure S2), which strongly proved the production of Cl₂ gas and supplemented the presence of the CuCl₂ decomposition reaction. From the above analysis, Cu²⁺ was converted to Cu⁺ in the process of doping Cu²⁺ into Rb₃InCl₆ by a vacuum solid-state reaction method, resulting in actual Cu⁺ doping.

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Figure 2. (a) The absorption spectra from the Kubelka–Munk transformation of a diffuse reflectance of pure-phase and Cu^+/Cu^{2+} -doped Rb_3InCl_6 . (b) The corresponding Tauc plots. The XPS spectra of Rb_3InCl_6 doped with (c) Cu^+ and (d) Cu^{2+} .



Figure 3. Variation of (a) PL peak position and (b) PLQY of Rb_3InCl_6 SCs with different Cu⁺ concentrations. (c) PLE and (d) PL spectra of pristine Rb_3InCl_6 and 5% Cu⁺-doped Rb_3InCl_6 . (e) The corresponding CIE diagram of the SCs under ultraviolet excitation. (f) TRPL decay curves.

The variation of PL peak position of Rb_3InCl_6 doped with different concentrations of Cu^+ ions is shown in Figure 3a and Table S3. As the doping concentration increased from 0 to 5%, the PL peak continued to blue-shift. With a further increase of

the Cu⁺ concentration to above 10%, the PL peak position remained unchanged, while an additional faint band appeared in the low-energy region with a peak at 465 nm (Figure S3), which might be due to the emission of Cu⁺ in the Rb₃InCl₆



Figure 4. Contour map of the variation of PL spectra with (a) excitation power density and (b) temperature of $Rb_3InCl_6:Cu^+$ SCs. The fitting curves of temperature-dependent (c) PL intensity and (d) fwhm of $Rb_3InCl_6:Cu^+$.

host material. Indeed, no traces of an additional impurity phase was detected in the PXRD patterns with Cu⁺ content in the reactants from 0 to 20% (Figure S4). In addition, compared with pristine Rb₃InCl₆ showing a PLQY of 8%, Rb₃InCl₆ doped with 5% Cu⁺ reached a maximum PLQY of 95%, indicating that the luminous efficiency was largely improved (Figure 3b). With a further increase of the Cu⁺ concentration, the PLQY of Rb₃InCl₆:Cu⁺ decreased gradually, with a value of 54% for a Cu⁺ doping concentration of 20%. Notably, 95% PLQY is the highest value among blue-violet emissive allinorganic 0D metal halides reported so far (Table S4). In the following, 5% Cu⁺-doped Rb₃InCl₆:Cu⁺ was selected for further investigation.

The PL excitation (PLE) and PL spectra of Rb₃InCl₆ and Rb₃InCl₆:Cu⁺ are shown in Figure 3c,d. The characteristic peak in the PLE spectra did not correspond to the absorption spectra, which fully indicated that the PL did not originate from the radiative emission induced by a band transition. Apparently, from the PL spectra, the pure-phase Rb₃InCl₆ exhibited a wide-band emission at 434 nm. After it was doped with Cu⁺, the emission peak blue-shifted to 398 nm, which is contrasted with the typical red-shift in the optical spectra with crystal lattice expansion.²⁸ The abnormal blue-shift of the PL should be related to a different emission mechanism after the Cu⁺ doping. Furthermore, the PL stability of Rb₃InCl₆:Cu⁺ under ambient conditions (20 °C, relative humidity 35%) was investigated. As shown in Figure S5, after a two month storage in air, the PL peak position remained unchanged, and the PL intensity still maintained 90% of the original value. The stability of Rb₃InCl₆:Cu⁺ is much better than that of the allinorganic Cu⁺-based halides. The high ambient stability of Rb₃InCl₆:Cu⁺ was further confirmed by PXRD, which showed

no obvious change in the diffraction pattern after two months (Figure S6).

From the measured excitation peak at 280 nm and the emission peak at 434 nm, the Stokes shift of pristine Rb_3InCl_6 was calculated to be 154 nm (1.57 eV). The large Stokes shift indicated the exciton recombination from STE states, which were developed through the interactions of excitons with the surrounding distorted lattice in the crystal structure. After the Cu⁺ doping, the Stokes shift reduced to a relatively small value of 118 nm (1.31 eV). Besides, from the PL spectra, the full width at half-maximum (fwhm) decreased from 88 to 54 nm, showing a narrower emission band after the doping.^{29,30} As shown in Figure 3e, the CIE color coordinates of Rb₃InCl₆ and Rb₃InCl₆:Cu⁺ were (0.16, 0.11) and (0.18, 0.06), respectively. The coordinate of Rb₃InCl₆:Cu⁺ was very close to the standard blue (0.15, 0.06), making it a potential material for pure blue light-emitting sources.

The PL decay dynamics were investigated by time-resolved PL (TRPL) measurements (Figure 3f, Table S3). The PL emissions of Rb₃InCl₆ and Rb₃InCl₆:Cu⁺ followed a mono-exponential decay. The PL lifetime increased from 6.85 μ s of pristine Rb₃InCl₆ to 13.95 μ s after a 5% Cu⁺ doping, suggesting that the introduction of Cu⁺ effectively suppressed the nonradiative recombination.³¹ However, the PL lifetime gradually decreased when the Cu⁺ content was more than 5%, which is consistent with the variation trend of PLQY (Table S3). This could be attributed to the more nonradiative decay pathways caused by excessive Cu⁺ ions. The ultralong PL lifetime and large Stokes shift indicated more excited-state structural reorganization in Rb₃InCl₆:Cu⁺, similar to the Cu(I)-complexed phosphors.³²

To understand the luminescence mechanism of $Rb_3InCl_6:Cu^+$ SCs, power- and temperature-dependent PL

properties were studied. The PL intensity of Rb₃InCl₆:Cu⁺ increased linearly with the excitation power density (Figures 4a and S7), indicating that the emission was not due to permanent defects.³³ The variation of PL spectra of Rb₃InCl₆:Cu⁺ with temperature in the range of 80–300 K is shown in Figure 4b. When the temperature was lowered from 300 to 80 K, the PL intensity of the emission peak around 398 nm (A band) increased continuously. A slight blue-shift of 6 nm in the PL peak position was observed, which was due to the lattice contraction. In addition, at low temperatures a new broad emission band appeared in the low-energy region with a peak at 640 nm (B band). As the temperature decreased, the PL intensity of both emission bands increased significantly due to the decrease in the nonradiative recombination. The bimodal PL emission indicated two types of radiative recombinations, probably due to the local structure distortions after Cu⁺ doping, leading to the low-energy emission band.

The variation of PL intensity (A band) with temperature was fitted using the following equation to obtain the exciton binding energy (Figure 4c)³⁴

$$I(T) = \frac{I_0}{1 + Ae^{-E_b/k_B T}}$$
(2)

where I(T) is the PL intensity at temperature T, I_0 is the initial value of the PL intensity, E_b is the exciton binding energy, and k_B is the Boltzmann constant. The exciton binding energy of Rb₃InCl₆:Cu⁺ showed a high value of 138.8 meV, which is significantly higher than 21.3 meV of the pristine Rb₃InCl₆ (Figure S8). The high exciton binding energy was favorable for a strong radiative recombination.³⁵

The variation of fwhm of the PL peak (A band) with temperature was further analyzed (Figure 4d). The fwhm decreased gradually, when the temperature was lowered, due to the reduction of the phonon vibrational energy. The relationship between fwhm and temperature was fitted using the following equation

$$\Gamma(T) = \Gamma_0 + \sigma T + \frac{\Gamma_{\rm LO}}{e^{h\omega_{\rm LO}/k_{\rm B}T} - 1}$$
(3)

where $\Gamma(T)$ represents the fwhm at temperature T (K), Γ_0 is the inhomogeneous broadening, σ refers to the interaction between the exciton and acoustic phonons and is usually negligible, $h\omega_{\rm LO}$ is the energy of longitudinal optical (LO) phonon, and $\Gamma_{\rm LO}$ is the interaction between charge carriers and LO phonons. The extracted fitting values of Γ_0 , $\Gamma_{\rm LO}$, and $h\omega_{\rm LO}$ of Rb₃InCl₆:Cu⁺ were 260.5, 502.5, and 36.1 meV, respectively. The $\Gamma_{\rm LO}$ of Rb₃InCl₆:Cu⁺ was much larger than 328.4 meV of pristine Rb₃InCl₆ (Figure S8), indicating the enhanced exciton—phonon coupling after Cu⁺ doping.³⁶

The influence of Cu⁺ heterovalent doping on the structural change, electronic structures, and photophysical properties was further discussed. Although the ionic radii of Cu⁺ (0.77 Å) and In³⁺ (0.80 Å) were very close, the substitution of In³⁺ with Cu⁺ in the center of the $[InCl_6]^{3-}$ octahedra was energetically unfavorable. As mentioned above, Cu⁺ atoms preferred to locate in a four-coordinated geometry with halogen atoms, for example, Cs₃Cu₂I₅,¹⁵ MA₄Cu₂Br₆,³⁷ and CsCu₂X₃ (X = Cl, Br, I).³⁸ Furthermore, it is also unreasonable for Cu⁺ ions occupying the Rb⁺ sites, since the ionic radius of Rb⁺ (1.56 Å) is much larger than that of Cu⁺. By a careful analysis of the atomic spacing and bond angle in the structure, when Cu⁺ is introduced into Rb₃InCl₆, the possible structure of Cu⁺ ions

would be local Cu-Cl clusters in the lattice, which leads to the local structural distortions and lattice expansion. DFT calculations were performed to understand the experimental observations. As shown in Figure S9, Rb₃InCl₆ shows a typical flat band as found in other 0D structures.^{22,39,40} The calculated projected density of states indicates that the valence band maximum (VBM) of the pristine Rb₃InCl₆ was mainly affected by the Cl 3p orbital. After the doping, the Cu 3d orbital contributed significantly to the VBM and promoted it to a higher-energy position, facilitating the exciton excitation in $Rb_3InCl_6:Cu^+$.⁴¹ The above discussions confirmed that Cu^+ doping played an important role in modulating the electronic band structure of Rb₃InCl₆. For pristine Rb₃InCl₆, upon a highenergy photoexcitation (280 nm), the electrons transferred from the singlet to triplet states, where they relaxed to the ground state with an intrinsic STE emission. After Cu⁺ was introduced, the photoinduced excitons were transferred to the triplet states of Cu⁺ by an ultrafast intersystem crossing process, and the efficient narrower-band blue-violet emission of Rb₃InCl₆:Cu⁺ was originated from the localized electronic transitions on the Cu⁺ sites, which were also influenced by the host crystal environment. The photophysical processes for Rb₃InCl₆ and Rb₃InCl₆:Cu⁺ were schematically illustrated in Figure 5. The reduction of the electronic dimension and



Configuration Coordinate

Figure 5. Schematic diagram of the emission mechanism.

enhanced exciton-phonon interactions as well as the electronic structure modulation in 0D Rb₃InCl₆:Cu⁺ resulted in the efficient radiative recombination and high PLQY. Our strategy of Cu⁺ doping balances the stability and optical properties of 0D Rb₃InCl₆ for further efficient luminescence applications.

In summary, we directly obtained Pb-free all-inorganic purephase Rb_3InCl_6 SCs via a vacuum solid-phase reaction method, with the crystal structure determined by SCXRD. To improve the luminous performance, both Cu⁺ and Cu²⁺ ions were incorporated into Rb_3InCl_6 . We found that the doping of Cu⁺ and Cu²⁺ resulted in the identical structure and optical properties due to the high-temperature decomposition of Cu²⁺ into Cu⁺ during the solid-state reaction. By Cu⁺ doping, the $Rb_3InCl_6:Cu^+$ showed a bright blue-violet emission with a peak at 398 nm and a greatly enhanced PLQY of 95%. Furthermore, the PL lifetime increased by ~2 times after the Cu⁺ doping.

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The improvement of PL emission was mainly due to the efficient electronic isolation and enhanced exciton—phonon coupling, as revealed by temperature-dependent PL measurements. From the structural analysis, Cu^+ ions acted as local clusters, thereby leading to the localization of excitons on the Cu^+ sites. The doping-induced enhanced luminous performance of Rb₃InCl₆:Cu⁺ was also related to the band structure modulation, as illustrated by DFT calculations. The expanding of the optical properties of Rb₃InCl₆:Cu⁺ with excellent stability further broadens applications of 0D metal halide SCs.

ASSOCIATED CONTENT

G Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c01751.

Experimental section; single-crystal data and structure refinement; bond lengths; EDS elemental mapping; SEM image; PL emission spectra; PXRD patterns; band structure, and PDOS (PDF)

Crystallographic information file of Rb₃InCl₆ (CIF)

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Notes

The authors declare no competing financial interest.

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