



Yb³⁺/Eu³⁺/Ho³⁺ Tridoped Cs₂Ag_{0.3}Na_{0.7}InCl₆ Double Perovskite with Excitation-Wavelength-Dependent Triple Emission for Anti-Counterfeiting Application

Qiaochu Chen ^{1,2}, Jialiang Jiang ², Hao Zhang ², Hui Fu ², Wenliang Liu ^{1,*} and Jinju Zheng ^{2,*}

- ¹ School of Packaging Design and Art, Hunan University of Technology, Zhuzhou 412007, China
- ² Institute of Micro/Nano Materials and Devices, Ningbo University of Technology, Ningbo 315211, China

* Correspondence: liuwenliang@hut.edu.cn (W.L.); jinjuzheng@nbut.edu.cn (J.Z.)

Abstract: Developing a secure anti-counterfeiting technology with more dimensional encryptions is urgently demanded. The lead-free double perovskite (DP) family represented by $A_2B_1B_{III}X_6$ hold great potential for applications in advanced fluorescence anti-counterfeiting owing to of large-bandgap engineering via B_I/B_{III} site transmutation or exotic dopants. Herein, Ln^{3+} ($Ln^{3+} = Eu^{3+}$, Ho^{3+} , and Yb^{3+})-doped $Cs_2Ag_{0.3}Na_{0.7}InCl_6$ DP microcrystals (MCs) were firstly successfully synthesized by a hydrothermal method. By selective excitation of different luminescence centrals through precise control of excitation wavelength, we demonstrate dynamic color tuning in the Ln^{3+} -doped $Cs_2Ag_{0.3}Na_{0.7}InCl_6$ DPMCs. Specifically, under various excitations of UV 300, 394, and NIR 980 nm, the as-synthesized DPMCs display triple emissions of warm yellow, red, and green, respectively. The warm yellow light stems from the self-trapped exciton (STE) downconversion (DC) luminescence of the DP matrix, while the red and green lights can be attributed to the strong $Eu^{3+}5D_0 \rightarrow ^7F_J$ (J = 1, 2, 3, 4) DC luminescence and Ho^{3+} ($^5F_4 \rightarrow ^5I_8$) upconversion (UC) luminescence sensitized by Yb^{3+} . Thus, the as-synthesized Ln^{3+} -doped $Cs_2Ag_{0.3}Na_{0.7}InCl_6$ DPMCs, which possess tunable combined DC/UC luminescence, show great potential to be an anti-counterfeiting material with a high security level.

Keywords: double perovskite; lanthanide ions (Ln³⁺); multimode luminescence; anti-counterfeiting

1. Introduction

The security of information and data has attracted great attention, and is closely related to anti-counterfeiting technology. Fluorescence anti-counterfeiting technology has been highlighted by a facile decryption process, simple device requirement, and huge information-loading capacity [1,2]. The traditional single-mode fluorescent anti-counterfeiting, which is usually achieved by downconversion (DC) luminescence, shows inadequate security for high-level data and information due to its simple technical barriers. Thus, developing reliable luminescent materials with multiple colors and tunable luminescence by simultaneously combining DC and upconversion (UC) luminescence has become an important but challenging topic for increasing the security of anti-counterfeiting technology [1].

Lead halide perovskite is expected to be the newcomer material for anti-counterfeiting because of its excellent optical properties including tunable bandgap, low-cost solution synthesis, and defect tolerance [3,4]. Unfortunately, these materials suffer from the two drawbacks of the toxicity of Pb and their poor stability. The lead-free double perovskite (DP) family represented by $A_2B_IB_{III}X_6$ has thus garnered particular interest in recent years due to its environmentally friendly nature and long-term operation, and especially enabling of large-bandgap engineering via B_I/B_{III} site transmutation or exotic dopants [1,5]. The doping of metal ions with s- and d-electrons in DPs, which can provide multiple emission centers, is considered one of the most common methods for achieving multicolor emission



Citation: Chen, Q.; Jiang, J.; Zhang, H.; Fu, H.; Liu, W.; Zheng, J. Yb³⁺/Eu³⁺/Ho³⁺ Tridoped Cs₂Ag_{0.3}Na_{0.7}InCl₆ Double Perovskite with Excitation-Wavelength-Dependent Triple Emission for Anti-Counterfeiting Application. *Crystals* **2023**, *13*, 13. https://doi.org/10.3390/ cryst13010013

Academic Editor: Dmitry Medvedev

Received: 28 November 2022 Revised: 16 December 2022 Accepted: 19 December 2022 Published: 22 December 2022



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). by DC luminescence. Typically, the emission color of Sb^{3+} and/or Mn^{2+} doped $Cs_2NaInCl_6$ DPs can be tuned from yellow to red or blue [6,7]. However, the simultaneously achieved DC and UC luminescence in perovskite materials, which is highly important for increasing the security level, is still rarely obtained [8–10]. To achieve the goal, lanthanide ions (Ln^{3+}) are considered an ideal candidate due to their unique 4f electronic configurations and rich UC energy-level structures. Moreover, doping rare earth ions in DPs can be easily achieved due to their similar ionic radius and valence state, as well as the preferred coordination number (CN) of 6 (same as trivalent metal cations in DPs) [11–14], which have achieved their prospective applications in light-emitting diodes (LEDs) and near-infrared bioimaging, etc. [14–18]. Thus, lanthanide ions doped DPs can be expected to be one of the most promising anti-counterfeiting materials for achieving multicolor emission with both DC and UC luminescence, which has rarely been studied until now.

The f–f transitions in Ln³⁺ usually exhibit a very low absorption coefficient due to the forbidden f–f transition [19], which was generally overcome by the codoping of sensitizers in phosphors such as Yb³⁺. Yb³⁺ has a large absorption coefficient near 980 nm and the energy can be effectively transferred to activators such as Ho³⁺, Er³⁺ for achieving UC luminescence [8,17,20,21], which is largely attributed to the feature of the single-transition channel of ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ in Yb³⁺ ion [22]. To achieve multicolor emission with both DC and UC luminescence, herein lead-free Yb³⁺/Eu³⁺/Ho³⁺ tridoped DPs are developed as high-security anti-counterfeiting material that exhibits trimodal luminescence of warm yellow, red, and green under light excitations at 300, 394 and 980 nm, respectively. The warm yellow emission observed in Cs₂Ag_{0.3}Na_{0.7}InCl₆: Yb³⁺/Eu³⁺/Ho³⁺ can be attributed to the self-trapped exciton (STE) emission of the DP matrix, while the red and green emissions originate from the strong transitions of ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 1, 2, 3, 4) of Eu³⁺ and ${}^{5}F_{4} \rightarrow {}^{5}I_{8}$ of Ho³⁺, individually. In addition, the effect of the doping concentration of Ln³⁺ on the optical properties and the corresponding photon relaxation dynamics of as-prepared Cs₂Ag_{0.3}Na_{0.7}InCl₆: Yb³⁺/Eu³⁺/Ho³⁺ are also systemically investigated.

2. Materials and Methods

Materials: Cesium chloride (CsCl, Macklin, 99.99%, Shanghai, China), silver chloride (AgCl, Macklin, 99.5%, Shanghai, China), sodium chloride (NaCl, Macklin, 99.5%, Shanghai, China), indium chloride (InCl₃, Macklin, 99.99%, Shanghai, China), Europium(III) chloride hexahydrate (EuCl₃·6H₂O, Macklin, 99.9%, Shanghai, China), holmium chloride hexahydrate (HoCl₃·6H₂O, Macklin, 98%, Shanghai, China) and Ytterbium(III) chloride hexahydrate (YbCl₃·6H₂O, Macklin, 98%, Shanghai, China) were used without further purification.

Synthesis of Cs₂Ag_{0.3}Na_{0.7}InCl₆:100%Yb³⁺, 50%Eu³⁺, 50%Ho³⁺ Microcrystals (MCs): As shown in Figure S1 (see supplementary), firstly, CsCl (2 mmol), AgCl (0.3 mmol), NaCl (0.7 mmol), InCl₃ (1 mmol), EuCl₃·6H₂O (0.5 mmol), HoCl₃·6H₂O (0.5 mmol), YbCl₃·6H₂O (1 mmol) and HCl (12 mL, 10 M) were added in a 25 mL Teflon autoclave. Then, the mixture solution was magnetically stirred vigorously for 30 min at room temperature. The sealed stainless-steel reactor was heated to 180 °C and kept for 12 h. The reactor was cooled to room temperature at a speed of 5 °C h⁻¹. The as-synthesized MCs were washed with isopropanol three times and then placed on the filter paper for natural drying. The dried samples were ground with a mortar for further characterization.

Characterization: The structure, morphology, and composition of the MCs were characterized by field-emission scanning electron microscopy (SEM, S-4800, Hitachi, Tokyo, Japan), X-ray diffraction (XRD, D8 Advance, Bruker, Karlsruhe, Germany), and transmission electron microscopy (TEM, JEM-2100F, JEOL, Tokyo, Japan). The UV-vis absorption spectra of the phosphors were recorded on a UV-visible spectrophotometer (Hitachi UV-3900, Tokyo, Japan). The steady-state PL, PLE spectra, and PL QYs were recorded using a spectrometer (Fluromax-4P, Horiba Jobin Yvon, Paris, France) equipped with a QY accessory. The PL decay curves were recorded on a spectrometer(FLS1000, Edinburgh Instruments, Livingston, Britain).

3. Results and Discussion

Figure 1a presents the typical SEM image of $Cs_2Ag_{0.3}Na_{0.7}InCl_6$: $Yb^{3+}/Eu^{3+}/Ho^{3+}$ MCs, and a truncated octahedral morphology with grain sizes of ~2–5 µm can be determined. The diffraction rings in the selected area electron diffraction (SAED) pattern (Figure 1b) can be assigned to (222), (331), (521), and (800) crystal planes of the sample, which have high accordance with the XRD result. The HRTEM image exhibits a legible lattice fringe for the (331) plane with an interplanar distance of 0.248 nm, indicating the high crystallinity of the sample (Figure 1c). The EDX spectrum (Figure S2) indicates the present of Cs, Ag, Na, In, Eu, Ho, Yb and Cl in the Cs₂Ag_{0.3}Na_{0.7}InCl₆: Yb³⁺/Eu³⁺/Ho³⁺ MCs, and the uniform distribution of above elements are further confirmed by the EDX mapping images, as shown in Figure 1d–l, which indicates that the Ln³⁺ are successfully doped into Cs₂Ag_{0.3}Na_{0.7}InCl₆ matrix without obvious aggregation.



Figure 1. (a) SEM image, (b) SAED pattern, (c) HRTEM image, and (d–l) EDX elemental mappings (Cs, Ag, Na, In, Cl, Eu, Ho, and Yb) of $Cs_2Ag_{0.3}Na_{0.7}InCl_6$: Yb³⁺/Eu³⁺/Ho³⁺ MCs.

Powder XRD characterization is performed to determine the crystallinity and phase purity of the as-prepared Ln³⁺-doped/undoped Cs₂Ag_{0.3}Na_{0.7}InCl₆ DPs. As presented in Figure 2, all samples exhibit obvious diffraction peaks, which correspond to the cube phases of Cs₂Ag_{0.3}Na_{0.7}InCl₆ (JCPDS No. 74-0484), meaning the phase structure of the matrix can be retained after doping. It is worth noting that all of the diffraction peaks are sharp and without any additional peaks after doping, indicating their excellent crystallinity and high purity [19]. The split XRD peaks observed between 40° and 55° can be confirmed as the overlapped two peaks corresponding to pure Cs₂Ag_{0.3}Na_{0.7}InCl₆ host and the tridoped Cs₂Ag_{0.3}Na_{0.7}InCl₆ MCs, meaning the presence of a mixed phase in the asprepared tridoped $Cs_2Ag_{0.3}Na_{0.7}InCl_6$ sample, which should be further optimized by precisely controlling the reaction parameters. Ln³⁺ of Yb³⁺ (0.86 Å), Eu³⁺ (0.95 Å), and Ho³⁺ (0.9 Å) can replace In³⁺ (0.8 Å), Na⁺ (1.02 Å) or Ag⁺ (1.15 Å) theoretically. The replacement of Na⁺ and Ag⁺ by Yb³⁺/Eu³⁺/Ho³⁺ will induce the shift of the diffraction peaks to a lower angle, which is inconsistent with our situation [23]. Thus, the In^{3+} in $Cs_2Ag_{0.3}Na_{0.7}InCl_6$ will be preferentially replaced by Yb³⁺/Eu³⁺/Ho³⁺ attributable to the similarity of ionic radii and ionic charges, which can be confirmed by the undetectable shift of the diffraction peak in our case.



Figure 2. XRD patterns of $Cs_2Ag_{0.3}Na_{0.7}InCl_6$: Yb³⁺/Eu³⁺/Ho³⁺ MCs and the standard XRD pattern of $Cs_2NaInCl_6$. The molar ratios of Yb:In, Eu:In, and Ho:In are 1:1, 1:1, and 0.6:1, respectively.

Figure 3 shows the absorption spectra of Ho³⁺/Yb³⁺ co-doped, Eu³⁺/Yb³⁺ co-doped, and Yb³⁺/Eu³⁺/Ho³⁺ tridoped Cs₂Ag_{0.3}Na_{0.7}InCl₆ DPs in the range of 350–1350 nm. The transition of the Eu³⁺, Ho³⁺, and Yb³⁺ from the ground states to the excited states is identified by the characteristic lines in the absorption spectra. It can be observed that the absorption peak at 960 nm (marked as 9) is the ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ transition of Yb³⁺ (Figure 3a). The characteristic absorption bands centered at 417, 452, 483, 538, 642, and 1150 nm corresponding to the transitions of Ho³⁺ from the ground state of ${}^{5}I_{8}$ to the excited states of ${}^{5}G_{5}$, ${}^{5}G_{6}$, ${}^{5}F_{3}$, ${}^{5}F_{4}$, ${}^{5}F_{5}$ and ${}^{5}I_{6}$, respectively (Figure 3b). Meanwhile, the absorption bands centered at 390 and 472 nm (marked as 1 and 2) can be ascribed to the transition of Eu³⁺ from the ground state of ${}^{7}F_{0}$ to the excited states of ${}^{5}D_{2}$ and ${}^{5}D_{1}$ (Figure 3c). The absorption bands of Ho³⁺/Eu³⁺/Yb³⁺ can be observed in Yb³⁺/Eu³⁺/Ho³⁺ tridoped sample, suggesting the successful doping of Yb³⁺/Eu³⁺/Ho³⁺ ions into the Cs₂Ag_{0.3}Na_{0.7}InCl₆ host.



Figure 3. UV-vis absorption spectra of $Cs_2Ag_{0.3}Na_{0.7}InCl_6$: $Yb^{3+}/Eu^{3+}/Ho^{3+}$ (**a**), $Cs_2Ag_{0.3}Na_{0.7}InCl_6$: Ho^{3+}/Yb^{3+} (**b**) and $Cs_2Ag_{0.3}Na_{0.7}InCl_6$: Eu^{3+}/Yb^{3+} (**c**) powder. The molar ratios of Yb:In, Eu:In, and Ho:In are 1:1, 1:1, and 0.6:1, respectively.

Two groups of samples are rationally designed to study the luminescence mechanism of as-prepared Yb³⁺/Eu³⁺/Ho³⁺ tridoped Cs₂Ag_{0,3}Na_{0,7}InCl₆ DPs. For the first series, the molar concentration ratios (all relative to In^{3+}) of Yb³⁺ and Eu³⁺ are both fixed at 100%, while that of Ho³⁺ is varied from 20% to 100% (Figure 4a,c,e). In the second series, the concentrations of Eu³⁺ and Ho³⁺ are varied while keeping the total ratio of 100% unchanged (Figure 4b,d,f). As shown in Figure 4a,b, a broad emission band located in the 320–720 nm range with a PL quantum yield (QY) of 28.1% is observed under the excitation of UV 300 nm, which derived from the STEs of the $Cs_2Ag_{0.3}Na_{0.7}InCl_6$ matrix with an average decay lifetime of 5.304 µs, is similar to that found in other lead-free double perovskites (Figure S4) [12,24], while the narrow emission bands at around 490, 542, 650, 590, 615, and 698 nm can be attributed to the transitions of $\text{Ho}^{3+5}\text{F}_3 \rightarrow {}^5\text{I}_8, {}^5\text{F}_4 \rightarrow {}^5\text{I}_8, {}^5\text{F}_5 \rightarrow {}^5\text{I}_8$ and $Eu^{3+5}D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_2$, ${}^5D_0 \rightarrow {}^7F_4$, respectively. The STE emission decreases sharply with increasing Eu^{3+} concentration (Figure 4a,b), suggesting the presence of an energy transfer from the host to the energy levels of the Eu³⁺ [25,26], leading to the competition PL between Eu³⁺ and STE. The emission band peaked at 650 nm can be attributed to ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ of Ho³⁺ rather than the Eu³⁺, which otherwise would have other characteristic transitions of Eu³⁺ in the PL spectra. Furthermore, a sharp concave peak can be seen at 540 nm in Figure 4a,b, and the concave peak is more obvious in the samples with heavier Ho^{3+} doping, which seems due to the ${}^{5}I_{8} \rightarrow {}^{5}F_{4}({}^{5}S_{2})$ resonance absorption of Ho³⁺. Under the excitation of UV 394 nm (Figure 4c,d), the Eu^{3+} ions can be directly excited to generate Eu^{3+} characteristic red emissions, which exhibit strong $Eu^{3+5}D_0 \rightarrow {}^7F_I$ (J = 1,2) emissions peaked at 590 and 615 nm, and weak transitions of ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ (650 nm) and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ (698 nm) with a PL QY of 4.1%. The peak at 590 nm can be attributed to the magnetic-dipole transition, while the peaks at 615, 650, and 695 nm should correspond to the electric-dipole transitions, which will be allowed when the Eu³⁺ ions occupy the crystallographic site lack inversion symmetry [19,27]. In our case, the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ electric-dipole transition displays the strongest emission at 615 nm, which means the Eu^{3+} ions mainly occupy the crystallographic site which lacks inversion symmetry. The decay curve by monitoring the emission at 613 nm can be fitted by a signal exponential decay function with a lifetime of 108 µs (Figure S4), which suggests that the 4f electrons of the Eu³⁺ ions are well screened from surrounding defect sites, via the closed $5s^25p^6$ outer shell electrons of Eu³⁺ [25,26]. The PL intensity decreases with increasing Ho³⁺ concentration, indicating the suppressor effect of Ho³⁺ on the Eu³⁺ PL. Under the excitation of near-infrared laser (NIR) 980 nm (Figure 4e,f), the green UC luminescence from the Ho³⁺ (${}^{5}F_{4} \rightarrow {}^{5}I_{8}$) sensitized by Yb³⁺ dominated the emission spectra, the Yb³⁺ ions in the ground state can be excited to the ${}^{2}F_{5/2}$ level by absorbing 980 nm photons. Energy on the excited ${}^{2}F_{5/2}$ level Yb³⁺ ions can be transferred to the Ho³⁺ ions, result in the strong green emission for the DPs co-doped with Yb^{3+} and Ho^{3+} . Thus, the phenomenon of strong green emission is observed in the UC emission. Besides the green emission of Ho³⁺, the other typical emission peaked at 652 nm were observed, which origins from the transition ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ of Ho³⁺ and can be suppressed by the doping of Eu³⁺.

Figure 5a shows PLE spectra ($\lambda_{em} = 613 \text{ nm}$) of the samples with a fixed content of Eu³⁺ and increasing content of Ho³⁺. As shown, besides a broad band, many sharp peaks presented in the PLE spectra, confirming that the characteristic luminescence of Eu³⁺ emission peaked at 613 nm can be obtained by direct excitation of the Eu³⁺ in Cs₂Ag_{0.3}Na_{0.7}InCl₆ host, especially by the ⁷F₀→⁵D₃ transition at 394 nm. The PLE intensity gradually decreases with increasing Ho³⁺ concentration, which indicates the suppressed Eu³⁺ emission by the doping of Ho³⁺. In addition, the presence of the broad PLE band in the 240 to 330 nm range is due to the overlapped emission of host STEs and Ho³⁺ emission at 613 nm was monitored (Figure 4a) [20]. This speculation can be further confirmed by the PLE spectra detected at 570 nm as shown in Figure 5b, in which a similar PLE band range from 240 to 330 nm is presented. Figure 4b shows the PLE spectra of this series of samples detected at 570 nm. As shown, except the decreased PLE intensity with increasing Ho³⁺ concentration, no detectable spectra shift can be observed, which indicates that Ho³⁺ doping weakens but does not change the origination of STEs emission of the Cs₂Ag_{0.3}Na_{0.7}InCl₆ host [1].



Figure 4. PL spectra of $Cs_2Ag_{0.3}Na_{0.7}InCl_6$: Yb³⁺/Eu³⁺/Ho³⁺ under ultraviolet light excitation at wavelengths of 300 (**a**,**b**), 394 nm (**c**,**d**) and NIR laser radiation (980 nm) (**e**,**f**).



Figure 5. PLE spectra of Cs₂Ag_{0.3}Na_{0.7}InCl₆: Yb³⁺/Eu³⁺/Ho³⁺ (**a**) $\lambda_{em} = 613$ nm (**b**) $\lambda_{em} = 570$ nm.

Based on the above results, the possible PL mechanism for $Cs_2Ag_{0.3}Na_{0.7}InCl_6$: Yb³⁺/ Eu³⁺/Ho³⁺ for multimodal anti-counterfeiting application is shown in Figure 6. Under UV 300 nm excitation, the electrons of $Cs_2Ag_{0.3}Na_{0.7}InCl_6$: $Yb^{3+}/Eu^{3+}/Ho^{3+}$ can be excited from the ground states to the excited states, and excited electrons can be depopulated by the following three paths: converted to the STEs through nonradiative relaxation, energy transfers to Ho³⁺ and Eu³⁺, and in turn produces the yellow emission as shown in Figure 6a. Under excitation of UV 394 nm, the Eu³⁺ ions can also be directly excited to generate Eu^{3+} characteristic red emissions (Figure 6b). While Figure 6c shows the simplified energy diagram of Cs₂Ag_{0 3}Na_{0 7}InCl₆: Yb³⁺/Eu³⁺/Ho³⁺ DPs under excitation of NIR 980 nm. As shown, the Ho³⁺ is largely excited by the Yb³⁺through the energy transfer, which presents a larger infrared light absorption cross-section than that of Ho³⁺ [25]. In addition, the ground state of the Yb³⁺ can be excited to the ${}^{2}F_{5/2}$ level by absorbing 980 nm photons, and energy on the exciting ${}^{2}F_{5/2}$ level can be transferred to the Ho³⁺. The energy difference between the ${}^{5}I_{7}$ and ${}^{5}I_{6}$ levels of Ho³⁺ and the ${}^{7}F_{6}$ and ${}^{7}F_{0}$ levels of Eu³⁺ matches well. Thus, the phenomenon of the strong green emission accompanied by weakened red emission is observed in the UC emission with co-doped Yb³⁺ and Ho³⁺, and the red light in the range of 635–670 nm tends to be extinguished with increasing Eu³⁺ concentration by the resonant energy transfer process and transferred to the ${}^{7}F_{6}$ level of Eu³⁺. Therefore, strong green emissions can be obtained by the appropriate doping ratio of Eu^{3+} to Ho^{3+} [15].

Figure 7 shows the photographs of as-prepared DPMCs/toluene/polystyrene composite films under excitations of UV 254 nm, UV 365 nm, and NIR 980 nm, which was directly patterned the precursor solution on the black paperboard to create a film with "HUT" and "NBUT" icons with the thickness of ~68 μ m (Figure S3). Information encryption and decryption can be switched on and off using the patterned film to realize the purpose of anti-counterfeiting. The pattern is colorless under natural light (encryption), while the bright yellow (Figure 7a), red (Figure 7b), and green (Figure 7c) emissions are clearly distinguished under irradiations of UV 254 nm, UV 365 nm, and NIR 980 nm (decryption), respectively. The above results directly present the potential applications of Cs₂Ag_{0.3}Na_{0.7}InCl₆: Yb³⁺/Eu³⁺/Ho³⁺ materials in high-level anti-counterfeiting technology.



Figure 6. Energy-level diagrams of Cs₂Ag_{0.3}Na_{0.7}InCl₆: Yb³⁺/Eu³⁺/Ho³⁺ and the proposed luminescence mechanism (**a**) $\lambda_{ex} = 300$ nm (**b**) $\lambda_{ex} = 394$ nm (**c**) $\lambda_{ex} = 980$ nm.



Figure 7. Anti-counterfeiting images of $Cs_2Ag_{0.3}Na_{0.7}InCl_6$: 100%Yb³⁺/100%Eu³⁺/60%Ho³⁺. The pattern was excited under UV 254 nm (**a**), UV 365 nm (**b**), and NIR 980 nm (**c**).

4. Conclusions

In conclusion, we reported the design and the experimental synthesis of Yb³⁺/Eu³⁺/Ho³⁺ tridoped Cs₂Ag_{0.3}Na_{0.7}InCl₆ DPMCs with trimode luminescence for application in anticounterfeiting with high security. The successful doping of Yb³⁺/Eu³⁺/Ho³⁺ into the Cs₂Ag_{0.3}Na_{0.7}InCl₆ matrix was systematically confirmed by EDS and absorption spectra characterization. Under excitation of UV 300 nm, in addition to a broad STE emission with bright yellow, some narrow emission bands corresponding to Eu³⁺ and Ho³⁺ are also presented in the PL spectra, indicating the presence of energy transfer processes from exciton to Ho³⁺ and Eu³⁺. Under 394 nm excitation, Eu³⁺ has strong characteristic luminescence at 613 nm with red emission by directly absorbing the excitation light. Under 980 nm excitation, because the sublevels of Ho³⁺ and Yb³⁺ are more matched, Yb³⁺ absorbs two photons of 980 nm and then transfers energy to Ho³⁺, which makes Ho³⁺ relax from ⁵S₂ to ⁵F₄, then emitting the characteristic green light through the ⁵F₄→⁵I₈ transition. Finally, the as-synthesized Ln³⁺-doped Cs₂Ag_{0.3}Na_{0.7}InCl₆ DPMCs–toluene–polystyrene composite films yield tunable DC–UC combined luminescence by selective excitation of different luminescent centrals through precise control of excitation wavelength, showing great potential as an anti-counterfeiting material with high security.

Supplementary Materials: The following supporting information can be downloaded at https: //www.mdpi.com/article/10.3390/cryst13010013/s1. Figure S1: Schematic diagram of the preparation of Yb³⁺/Eu³⁺/Ho³⁺ tridoped Cs₂Ag_{0.3}Na_{0.7}InCl₆ double perovskite; Figure S2: The typical EDS spectrum of Yb³⁺/Eu³⁺/Ho³⁺ tridoped Cs₂Ag_{0.3}Na_{0.7}InCl₆ double perovskite; Figure S3: The thickness of Yb³⁺/Eu³⁺/Ho³⁺ tridoped Cs₂Ag_{0.3}Na_{0.7}InCl₆ anti-counterfeiting film; Figure S4: The emission decay curves obtained for Cs₂Ag_{0.3}Na_{0.7}InCl₆: Yb³⁺/Eu³⁺/Ho³⁺ MCs against the excitation wavelengths of (a)394 and (b) 300 nm by monitoring the emission at (a) 613 and (b) 570 nm.

Author Contributions: Conceptualization, Q.C.; Formal analysis, Q.C. and J.J.; Investigation, Q.C.; Resources, J.Z.; Writing—original draft, Q.C.; Writing—review & editing, H.Z., W.L. and J.Z.; Visualization, Q.C.; Supervision, J.Z.; Project administration, H.F.; Funding acquisition, J.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by "Science and Technology Innovation 2025" of Ningbo Foundation (grant 2020Z061), Zhejiang Provincial Nature Science Foundation (grant LGJ20E020002).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- Li, X.; Xu, S.; Liu, F.; Qu, J.; Shao, H.; Wang, Z.; Cui, Y.; Ban, D.; Wang, C. Bi and Sb Codoped Cs₂Ag_{0.1}Na_{0.9}InCl₆ Double Perovskite with Excitation-Wavelength-Dependent Dual-Emission for Anti-counterfeiting Application. *ACS Appl. Mater. Interfaces* 2021, 13, 31031–31037. [CrossRef] [PubMed]
- 2. Kumar, P.; Creason, T.D.; Fattal, H.; Sharma, M.; Du, M.H.; Saparov, B. Composition-Dependent Photoluminescence Properties and Anti-Counterfeiting Applications of A₂AgX₃ (A=Rb, Cs; X=Cl, Br, I). *Adv. Funct. Mater.* **2021**, *31*, 2104941. [CrossRef]
- 3. Ji, Y.; Wang, M.; Yang, Z.; Wang, H.; Padhiar, M.A.; Qiu, H.; Dang, J.; Miao, Y.; Zhou, Y.; Bhatti, A.S. Strong Violet Emission from Ultra-Stable Strontium-Doped CsPbCl₃ Superlattices. *Nanoscale* **2022**, *14*, 2359–2366. [CrossRef] [PubMed]
- Ji, Y.; Wang, M.; Yang, Z.; Ji, S.; Qiu, H.; Dou, J.; Gaponenko, N.V. Reversible Transformation between CsPbBr₃ Nanowires and Nanoparticles. *Chem. Commun.* 2019, 55, 12809–12812. [CrossRef] [PubMed]
- 5. Luo, J.; Wang, X.; Li, S.; Liu, J.; Guo, Y.; Niu, G.; Yao, L.; Fu, Y.; Gao, L.; Dong, Q. Efficient and Stable Emission of Warm-White Light from Lead-Free Halide Double Perovskites. *Nature* **2018**, *563*, 541–545. [CrossRef]
- Kaur, J.; Mondal, B.; Xia, Z.; Arfin, H.; Kshirsagar, A.S.; Nag, A.; Chakraborty, S. ns² Electron (Bi³⁺ and Sb³⁺) Doping in Lead-Free Metal Halide Perovskite Derivatives. *Chem. Mater.* 2020, 32, 10255–10267.
- Chen, L.; Yang, W.; Fu, H.; Liu, W.; Shao, G.; Tang, B.; Zheng, J. Mn²⁺-Doped Cs₂NaInCl₆ Double Perovskites and Their Photoluminescence Properties. J. Mater. Sci. 2021, 56, 8048–8059. [CrossRef]
- Li, S.; Hu, Q.; Luo, J.; Jin, T.; Liu, J.; Li, J.; Tan, Z.; Han, Y.; Zheng, Z.; Zhai, T. Self-Trapped Exciton to Dopant Energy Transfer in Rare Earth Doped Lead-Free Double Perovskite. *Adv. Opt. Mater.* 2019, *7*, 1901098. [CrossRef]
- 9. Jin, S.; Li, R.; Huang, H.; Jiang, N.; Lin, J.; Wang, S.; Zheng, Y.; Chen, X.; Chen, D. Compact Ultrabroadband Light-Emitting Diodes Based on Lanthanide-Doped Lead-Free Double Perovskites. *Light Sci. Appl.* **2022**, *11*, 52. [CrossRef]
- 10. Liu, N.; Zheng, W.; Sun, R.; Li, X.; Xie, X.; Wang, L.; Zhang, Y. Near-Infrared Afterglow and Related Photochromism from Solution-Grown Perovskite Crystal. *Adv. Funct. Mater.* **2022**, *32*, 2110663. [CrossRef]
- 11. Zeng, Z.; Huang, B.; Wang, X.; Lu, L.; Lu, Q.; Sun, M.; Wu, T.; Ma, T.; Xu, J.; Xu, Y. Multimodal Luminescent Yb³⁺/Er³⁺/Bi³⁺-Doped Perovskite Single Crystals for X-ray Detection and Anti-Counterfeiting. *Adv. Mater.* **2020**, *32*, 2004506. [CrossRef]
- 12. Nie, J.; Zhou, B.; Fang, S.; Zhong, H.; Li, H.; Shi, Y. Efficient Multicolor and White Photoluminescence in Erbium-and Holmium-Incorporated Cs₂NaInCl₆: Sb³⁺ Double Perovskites. *Chem. Mater.* **2022**, *34*, 6288–6295. [CrossRef]
- Liu, Y.; Rong, X.; Li, M.; Molokeev, M.S.; Zhao, J.; Xia, Z. Incorporating Rare-Earth Terbium (III) Ions into Cs₂AgInCl₆: Bi Nanocrystals toward Tunable Photoluminescence. *Angew. Chem. Int. Ed.* 2020, 59, 11634–11640. [CrossRef]
- 14. Arfin, H.; Kaur, J.; Sheikh, T.; Chakraborty, S.; Nag, A. Bi³⁺-Er³⁺ and Bi³⁺-Yb³⁺ Codoped Cs₂AgInCl₆ Double Perovskite Near-Infrared Emitters. *Angew. Chem. Int. Ed.* **2020**, *59*, 11307–11311. [CrossRef]
- Schmitz, F.; Guo, K.; Horn, J.; Sorrentino, R.; Conforto, G.; Lamberti, F.; Brescia, R.; Drago, F.; Prato, M.; He, Z. Lanthanide-Induced Photoluminescence in Lead-Free Cs₂AgBiBr₆ Bulk Perovskite: Insights from Optical and Theoretical Investigations. *J. Phys. Chem. Lett.* 2020, *11*, 8893–8900. [CrossRef]
- 16. Chen, N.; Cai, T.; Li, W.; Hills-Kimball, K.; Yang, H.; Que, M.; Nagaoka, Y.; Liu, Z.; Yang, D.; Dong, A. Yb-and Mn-Doped Lead-Free Double Perovskite Cs₂AgBiX₆ (X= Cl⁻, Br⁻) Nanocrystals. *ACS Appl. Mater. Interfaces* **2019**, *11*, 16855–16863. [CrossRef]

- 17. Lee, W.; Hong, S.; Kim, S. Colloidal Synthesis of Lead-free Silver–Indium Double-Perovskite Cs₂AgInCl₆ Nanocrystals and Their Doping with Lanthanide Ions. *J. Phys. Chem. C* 2019, *123*, 2665–2672. [CrossRef]
- Zhang, G.; Wei, Y.; Dang, P.; Xiao, H.; Liu, D.; Li, X.; Cheng, Z.; Lin, J. Facile Solution Synthesis of Bi³⁺/Yb³⁺ Ions Co-Doped Cs₂Na_{0.6}Ag_{0.4}InCl₆ Double Perovskites with Near-Infrared Emission. *Dalton Trans.* 2020, 49, 15231–15237. [CrossRef]
- 19. Nie, J.; Li, H.; Fang, S.; Zhou, B.; Liu, Z.; Chen, F.; Wang, Y.; Shi, Y. Efficient Red Photoluminescence in Holmium-Doped Cs₂NaInCl₆ Double Perovskite. *Cell Rep. Phys. Sci.* **2022**, *3*, 100820. [CrossRef]
- Lin, H.; Chen, D.; Yu, Y.; Shan, Z.; Huang, P.; Wang, Y.; Yuan, J. Nd³⁺-Sensitized Upconversion White Light Emission of Tm³⁺/Ho³⁺ Bridged by Yb³⁺ in β-YF₃ Nanocrystals Embedded Transparent Glass Ceramics. J. Appl. Phys. 2010, 107, 103511. [CrossRef]
- Wei, H.L.; Zheng, W.; Zhang, X.; Suo, H.; Chen, B.; Wang, Y.; Wang, F. Tuning Near-Infrared-to-Ultraviolet Upconversion in Lanthanide-Doped Nanoparticles for Biomedical Applications. *Adv. Opt. Mater.* 2022, 2022, 2201716. [CrossRef]
- 22. Dong, H.; Sun, L.-D.; Yan, C.-H. Energy Transfer in Lanthanide Upconversion Studies for Extended Optical Applications. *Chem. Soc. Rev.* **2015**, *44*, 1608–1634. [CrossRef] [PubMed]
- 23. Yang, S.; Gong, S.; Zhou, Z.; Wu, L.; Zhang, M.; Jiang, L.; Wu, W. Bi and Yb Codoped Cs₂Ag_{0.6}Na_{0.4}InCl₆ Microcrystals: Visible to Near-Infrared Fluorescence for Thermometry. *J. Phys. Chem. C* **2021**, *125*, 10431–10440. [CrossRef]
- 24. Liu, X.; Xu, X.; Li, B.; Yang, L.; Li, Q.; Jiang, H.; Xu, D. Tunable Dual-Emission in Monodispersed Sb³⁺/Mn²⁺ Codoped Cs₂NaInCl₆ Perovskite Nanocrystals Through an Energy Transfer Process. *Small* **2020**, *16*, 2002547. [CrossRef]
- Gao, W.; Dong, J.; Liu, J.; Yan, X. Effective Tuning of the Ratio of Red to Green Emission of Ho³⁺ Ions in Single LiLuF₄ Microparticle via Codoping Ce³⁺ Ions. J. Alloys Compd. 2016, 679, 1–8. [CrossRef]
- 26. Yao, M.M.; Wang, L.; Yao, J.S.; Wang, K.H.; Chen, C.; Zhu, B.S.; Yang, J.N.; Wang, J.J.; Xu, W.P.; Zhang, Q. Improving Lead-Free Double Perovskite Cs₂NaBiCl₆ Nanocrystal Optical Properties via Ion Doping. *Adv. Opt. Mater.* **2020**, *8*, 1901919. [CrossRef]
- Hu, Q.; Deng, Z.; Hu, M.; Zhao, A.; Zhang, Y.; Tan, Z.; Niu, G.; Wu, H.; Tang, J. X-ray Scintillation in Lead-Free Double Perovskite Crystals. Sci. China Chem. 2018, 61, 1581–1586. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.