White-Light-Emitting Control via Lead-free Perovskite Material

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Abstract. In recent years, the emerging lead-free halide perovskites are attracting great attention in the field of the optical detection and luminescence due to its inherent strong light absorption and high balanced carrier on transmission characteristics. This experiment attempts to explore the way of grinding to prepare the white light emitting materials that does not contain lead. Low dimensional lead-free copper-based halide luminescent materials are prepared by controlling the molar ratio of a series of lead-free perovskite materials Cs3Cu2I5 and CsCu2I3. As-synthesized powder samples are characterized by powder X-ray diffraction (XRD), photoluminescence spectrum (PL), photoluminescence excitation spectrum (PLE) and photoluminescence quantum yield (PLQY) and other characterization methods. We successfully prepare the white powder sample by controlling the molar ratio of reactants (CsI:CuI=1:3). We measure the Commission Internationale de l’Eclairage (CIE) chromaticity coordination of PL spectra for the samples which can be regulated by the ratio of reactants. Moreover, it is demonstrated that acetone can effectively promote the reaction of reactants. These findings make this material be a stable and environmentally friendly white luminescent material, which has the potential to be used in white LED applications.

1. Introduction  
Perovskite materials are initially used in the field of solar cells thanks to its outstanding performance of inherent strong light absorption and high balanced carrier transmission characteristics[1]. Perovskite materials have become a hot spot in scientific research. However, the traditional perovskite materials use Pb as the base material, and the commercialization of lead-based perovskite materials is limited due to the presence of Pb which is a toxic heavy element. Researchers began to use Cu2+ instead of toxic Pb2+ to prepare better stability and low toxicity of all inorganic copper-based materials[2]. It has been reported that Cs3Cu2I5 is a non-toxic perovskite material, which has 0-dimensional structure which provides wide-band blue emission (about 445 nm) and large Stokes shift, with a high fluorescence quantum yield of around 90%[3]. Lin et al. reported that the all-inorganic CsCu2I3 single crystal exhibited stable photoluminescence (PL) properties and had a 15.7% PLQY[4]. This experiment attempts to use CsI and CuI as reactants to explore the way of grinding to prepare the white light emitting materials[5]. While exploring the stability and low toxicity of this material, we try to study its luminescent properties.

2. Experimental part

2.1. Synthesis of the samples  
In this experimental synthesis, Cesium iodide (CsI 99.9%), copper iodide(I) (CuI 99.99%), acetone
The reagents used in this experiment are used directly without further treatment. We have controlled the molar ratio of reactants and the time of grinding. As shown in the Figure 1, we weigh CsI and CuI in a certain proportion, following which they are mixed in a mortar and grinding for a certain time. In order to verify the effect of acetone on the products, two groups of the experimental samples are divided. Samples 1, 4, 5, 6, 9, 10, 11 and 12 are added 200 μL acetone every two minutes during the grinding process (Table 1). Samples 2, 3, 7 and 8 are ground without acetone as a contrast experiment (Table 1). Six different proportions of reactants are set to control the ratio of Cs₃Cu₂I₅ and CsCu₂I₃ in the products to achieve the control of white light.

Figure 1. Flow chart of sample preparation. Fluorescence image of samples synthesized with different reactant ratios of CsI and CuI under UV light at 305 nm.

Table 1. The following table shows the number of samples which obtained by different grinding time and different molar ratio of reactants.

| Molar ratio (CsI:CuI) | Grinding Time | Sample Number | Grinding Time | Sample Number |
|----------------------|---------------|---------------|---------------|---------------|
| 3:1 (0.389 g and 0.095 g) | 4 min* | 1 | 10 min | 3 |
| 3:2 (0.389 g and 0.190 g) | 5 min | 2 | 4 min* | 5 |
| 1:1 (0.260 g and 0.095 g) | 4 min* | 4 | 6 | |
| 1:2 (0.260 g and 0.190 g) | 5 min | 7 | 10 min | 8 |
| 1:3 (0.260 g and 0.286 g) | 2 min* | 9 | 4 min* | 10 |
| 1:4 (0.260 g and 0.381 g) | 4 min* | 11 | | |

* Adds 200 μL acetone every two minutes of grinding.

2.2. Characterization and Electrochemical Measurements

The XRD patterns of the synthesized powder materials are characterized by Bruker D2 X-ray diffractometer, Photoluminescence spectra (PL), photoluminescence excitation spectra (PLE) and photoluminescence quantum yield (PLQY) is tested by Edinburgh instrument FS5 fluorescence spectrophotometer.
3. Result and Discussion

In order to detect the substance composition in the powder samples obtained from grinding, we characterize samples 2, 3, 4, 5 and 7, 8, 9, 10 by XRD respectively. When grinding without adding acetone, reaction becomes more sufficient as the grinding time increases, resulting the conversion of CuI in the reactants to Cs3Cu2I5. Figure 2(a) shows that the intensity of CuI diffraction peak is gradually decreased, while the intensity of Cs3Cu2I5 diffraction peak is gradually increased. The diffraction peak of CsCu2I3 does not appear in the XRD. It implicates that the sample did not contain CsCu2I3. Compared the XRD patterns of the sample grinding for 4 minutes with acetone and the sample grinding for 10 minutes without acetone, the diffraction peak of CuI at 25 degree is even weaker and the intensity of the diffraction peaks of CsCu2I3 becomes stronger. Figure 2(b) also shows this trend. As the grinding time increases, more CuI will be reacted into CsCu2I3. The intensity of the diffraction peak of CuI shown in the graph decreases, while the peak of CsCu2I3 increases. CuI diffraction peak of the sample after grinding with acetone for four minutes is weaker than that of the sample after grinding for ten minutes without adding acetone. This fully demonstrates that the reactant CuI and CsI react more adequately and the reaction is carried out to a higher degree when the reaction time is increased or acetone solvent is added. The result suggests that a small amount of acetone does not cause the decomposition of halogenated perovskite, but rather promotes the reaction of CuI and CsI to proceed faster.

By comparison with the analysis in Figure 2(a) and Figure 2(b), it is shown that with the gradual decrease of the mole ratio of reactant CsI, the diffraction peaks of CsCu2I3 are enhanced, while the diffraction peaks of Cs3Cu2I5 are gradually weakened. This indicates that, as the molar ratio of CuI in the reactants increases, the proportion of CsCu2I3 in the products increases, and the corresponding proportion of Cs3Cu2I5 decreases. However, it can be found that the diffraction characteristic peak of CsI is also found in the XRD spectrum when the molar ratio of the reactants is 1:2. Therefore, the two reactants of CsI and CuI have not fully reacted, and we need to further expand the molar ratio of the reactants to achieve the control of white light.

Figure 2. XRD patterns of samples 2, 3, 4, 5(a) and samples 7, 8, 9, 10(b), as well as CsI, CuI, Cs3Cu2I5 and CsCu2I3 characteristic peaks of XRD. Pink dots represent CsI (JCPDS, No. 77-2185) and purple pentagons represent CuI. Brown diamonds indicate the diffraction peaks of Cs3Cu2I5 (JCPDS, No. 79-0333) and green triangles indicate the peaks of CsCu2I3 (JCPDS, No. 77-0069).

Figure 3 shows the excitation spectra (PLE) of sample 7 which is tested at λem = 440 nm for Cs3Cu2I5 and 580 nm for CsCu2I3 respectively. The excitation peak of perovskite Cs3Cu2I5 is around 330 nm, while there is a blue-shift of the excitation peak of perovskite Cs3Cu2I5 and the excitation peak moves to about 305 nm. Therefore, it fully demonstrates the presence of Cs3Cu2I5 and CsCu2I3 in sample 7. We have proved that acetone can speed up this kind of reaction to a certain extent. Because the perovskite Cs3Cu2I5 and CsCu2I3 can emit blue and yellow light respectively[6], we can adjust the ratio of Cs3Cu2I5 and CsCu2I3 in the product by adjusting the molar ratio of reactants, so as to further achieve the purpose of controlling the white light.
Figure 3. Photoluminescence excitation (PLE) spectra of the as-synthesized sample 7 (CsI:CuI =1:2) with $\lambda_{\text{em}} = 440$ nm and 580 nm respectively.

Figure 4. (a) XRD patterns of samples 1, 5, 6, 10, 11, 12 as well as Cs$_3$Cu$_2$I$_5$ and CsCu$_2$I$_3$ characteristic peaks of XRD. Blue triangles indicate the diffraction peaks of Cs$_3$Cu$_2$I$_5$ (JCPDS, No. 79-0333) and pink dots indicate the peaks of CsCu$_2$I$_3$ (JCPDS, No. 77-0069). The dotted lines represent the diffraction peak of CuI. (b) Photoluminescence emission (PL) spectra of samples 1, 5, 6, 10, 11, 12, and photoluminescence photos of samples 1, 5, 6, 10, 11, 12 with different molar ratios of CsI and CuI under UV illumination (305 nm light).

In order to achieve better control of the white light, the molar ratio of CuI in the reactants is further expanded. Samples 1, 5, 6, 10, 11, 12 are then characterized by XRD and PL spectra. As shown in Figure 4 (a), with the increase of the mole ratio of CuI in the reactants, the strength of the characteristic peak of Cs$_3$Cu$_2$I$_5$ contained in the sample is gradually decreasing, and correspondingly, the characteristic peak of CsCu$_2$I$_3$ contained in the sample shows an increasing trend. PL spectra of the samples 1, 5, 6, 10, 11, 12 (Figure 4(b)) shows the broadband spectra which indicate the presence of both CsCu$_2$I$_3$ (about 580 nm)$^7$ and Cs$_3$Cu$_2$I$_5$ (around 440 nm)$^7$. With the increase of Cs$_3$Cu$_2$I$_5$ contained in the sample, the peak at 580 nm gradually becomes stronger, and the peak near 440 nm weakens correspondingly. Broadband white light covers most of the full visible spectrum. As shown in Figure 4(b), the colors of the samples gradually change from dark blue light to cold white light under the light excitation of 305 nm, and then change again toward the trend of warm white light.
Finally, we detect the Photoluminescence quantum yield (PLQY) of samples 11 and 12 (as shown in Figure 5 (a)), which are 12.46% and 8.89% respectively. Although Cs$_3$Cu$_2$I$_5$ can be considered to provide broadband blue emission and large Stokes shift, with a high PLQY of 90%, the PLQY of CsCu$_2$I$_3$ which is yellow fluorescence, is not high with only 15.7%. This reason causes the low PLQY of the samples 11 and 12. Finally, we measure the Commission Internationale de l’Eclairage (CIE) chromaticity coordination of PL spectra for the samples (Figure 5). The CIE coordinate of sample 11 (molar ratio 3:1) is (0.32,0.33) in the white light area as shown in Figure 5(b), which are approaching the ideal pure white emission coordinates (0.33, 0.33) [8].

4. Conclusions
In summary, we successfully prepares the white powder sample by controlling the molar ratio of reactants (CsI:CuI=1:3). It is demonstrated that acetone can effectively promote the reaction of reactants. The results of XRD and PL spectra show that by controlling the ratio of CsI and CuI in the reactants, the color of the samples gradually change from deep blue light to cold white light, and then change again toward the trend of warm white light under the excitation of 305nm light. And this approach hopefully achieves full coverage in visible light. Moreover, this material can be stable in the air for around three weeks. However, the fluorescence quantum yield of this material is only 12.46%. We need to do further work to improve its PLQY. These findings make this material be a stable and environmentally friendly white luminescent material, which has the potential to be used in white LED applications.

Acknowledgments
This work was financially supported by the grants from Guangdong Basic and Applied Basic Research Foundation (Grant no: 2019A1515011762), Shenzhen Science and Technology Innovation Foundation (Grant no: JCYJ20180305125302333, JCYJ20170818093035338, JCYJ201803051254309 54), Shenzhen University Fund (Grant no: 860-000002110229) and Foshan City Education Department Foundation.

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