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Warm white light-emitting diodes using organic–inorganic halide perovskite materials coated YAG:Ce^{3+} phosphors

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ABSTRACT

This work reports warm white light-emitting diodes (WLEDs) using organic–inorganic halide perovskite materials coated YAG:Ce^{3+} phosphors by a liquid phase synthesis method. The perovskite $MAPbBr_{3-x}I_x$-coated YAG:Ce^{3+} phosphors have more red light contribution than YAG:Ce^{3+} phosphors without the perovskite coating. The chromaticity coordinate of white LED with YAG:Ce^{3+} remote phosphor is (x = 0.3134, y = 0.3497) 6359. However, those of $MAPbBr_{2.5}I_{0.5}$ and $MAPbBr_{2.0}I_{1.0}$-coated YAG:Ce^{3+} remote phosphor shift to (x = 0.4220, y = 0.3725) 2908 and (x = 0.4067, y = 0.4028) 3525, respectively. The colors of perovskite-coated samples are more red and warm. Therefore, the perovskite-coated YAG:Ce^{3+} method is useful for warm WLED.

1. Introduction

White light-emitting diodes (WLEDs) have developed for solid-state lighting due to their high luminosity, high energy conversion efficiency and long lifetime [1–4]. Up to now, the combination of a blue-emitting GaN light-emitting diode (LED) and yellow phosphors $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce^{3+}) is most commonly used as WLEDs. However, high correlated color temperature (CCT) or low color rendering index (CRI) is obtained in the devices due to insufficient red light contribution, which limits their certain applications, such as indoor lighting. Several techniques have been developed to increase the CRI or decrease the CCT. The most popular method is that red phosphors are introduced into the blue LED and YAG:Ce^{3+} system to enhance the red region of the spectral emission characteristics of YAG:Ce^{3+}. Red phosphors such as nitride [5,6] ($B_2Si_5N_8:Eu^{2+}$ and $BAlSiN_3:Eu^{2+}$ (B = Ca, Sr and Ba)) and fluoride [7–10] (A_2AlF_6: Mn^{4+} and A_3DF_6: Mn^{4+} (A = Li, Na, K and Rb; D = Si, Ge, Sn)) are widely used in warm WLED devices. However, this method requires extra red phosphors, resulting in complex processes and higher cost.

On the other hand, organic halide perovskites materials have drawn a great deal of attention due to their potential in photovoltaic [11–13] and light-emitting devices [14–16]. They can be prepared by low-cost and low-temperature solution processes and still exhibit large absorption coefficients, ultralow bulk defect densities and slow Auger recombination [17], which are attractive for a wider range of the practice optoelectronic applications [18]. Their visible photoluminescence (PL) tunability (400–800 nm) can be straightly achieved by halide ion substitution in $CH_3NH_3PbX_3$ chemical structures (or $MAPbX_3$) [17,19]. Therefore, it is interesting to employ excellent characteristics of the perovskite materials to improve CRI and CCT of the WLEDs.

Herein, we report another method, which potentiates the spectra of YAG:Ce^{3+} phosphors using organic–inorganic halide perovskites materials, to enrich the red light emission region. The method employs a simple and rapid grinding process to coat $CH_3NH_3PbBr_{2.5}I_{0.5}$ and $CH_3NH_3PbBr_{2.0}I_{1.0}$ on the surface of the YAG:Ce^{3+} powders, which requires very low material cost and no high temperature sintering treatments The warm WLEDs based on the perovskite materials have also demonstrated, leading the improved CCTs compared to the traditional YAG:Ce^{3+} based WLEDs.

2. Experiments

Methylammonium bromide (MABr; Lumtec.Inc.), Methylammonium iodide (MAI; Lumtec. Inc.), $PbBr_2$ (Sigma-Aldrich. Inc.), and PbI_2 (Sigma-Aldrich. Inc.) were dissolved in dimethylformamide (DMF) by mixing an molar ratio of 1:1-x:x as a $MAPbBr_{3-x}I_x$ precursor solution of 0.3 M. All of them were directly used without any further purification. The perovskite precursor solution (10 μL) was drop onto YAG:Ce^{3+} powder (Titec Corporation Ltd., 0.2 g) placed in an agate mortar and then they were grounded by using an agate pestle. During grindings, small amount of DMF was added to mix the raw materials homogenously. The processing flow diagram was shown in Fig. 1. After grindings, the mixed powders dried at room temperature for 3 h in the air. The perovskite coated YAG:Ce^{3+} powder can be easy and rapid fabrication, which showed in the supporting video file ($MAPbBr_{2.5}I_{0.5}$-coated YAG powders). The crystalline characteristics of the powder were observed by PANalytical X'Pert Pro DY2840 X-ray

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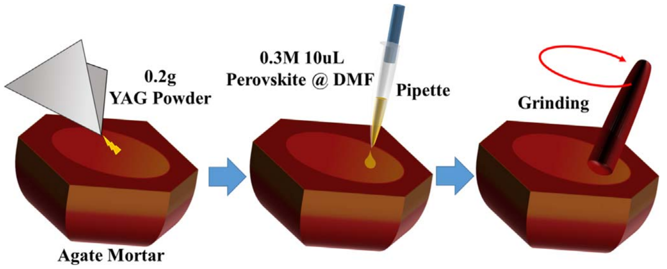

Fig. 1. Flow process diagram for perovskite-coated YAG powders.

diffraction with Cu-Kα radiation. A field emission scanning electron microscope (FESEM; GeminiSEM, ZEISS)) was adopted to examine the morphology and size of the powders. A CW DPSS laser emitting at 266 nm and fluorescence spectrophotometer (Hitachi F-7000) were used for photoluminescence (PL) measurements.

3. Results and discussion

Fig. 2(a) presents the pictures of various perovskite powders. The color of the powder is from yellow, amber, orange, brown to black when the content of Cl decreases and the content of I increase. Fig. 2(b) shows the photographs of these powders excited with 266 nm laser. The colors present bluish green, cyan, green, orange, red, and purple. They are different to the pictures of Fig. 2(a). Fig. 3 shows the photoluminescence (PL) spectra of various perovskite powders. The locations of peaks of PL spectra are 490, 535, 550, 680, 715, and 765 nm, respectively. The purpose of this work is to produce a warm white LED. Therefore, the MAPbBrI series powders are favorite phosphors.

Fig. 4 shows photographs of YAG:Ce^{3+} phosphor powder and $MAPbBr_{3-x}I_x$-coated YAG:Ce^{3+} powders with the element contents x = 0.5, 1.0, and 1.5. The different color of YAG:Ce^{3+}powders with and without perovskite coating can been clearly observed by naked eye. The emitting lights of all samples excited under a 266 nm laser also have distinguishable colors. The color and PL of the powders more approaches red with increasing I content, which is due to the reduced bandgaps of perovskites. This indicates that the colors of $MAPbBr_{3-x}I_x$ coated on YAG:Ce^{3+} powders can be tuned easy using the different element ratio of I to Br.

Figs. 5(a) and 4(b) show FESEM images of pure YAG:Ce^{3+} powders and $MAPb_{2.5}I_{0.5}$–coated YAG:Ce^{3+} powders, respectively. Particle size of YAG:Ce^{3+} powders and $MAPbBr_{2.5}I_{0.5}$-coated YAG:Ce^{3+} powders are similar according to the FESEM images. This means the thickness of the $MAPbBr_{2.5}I_{0.5}$ coated on YAG:Ce^{3+} particles by liquid phase synthesis method is very thin. Also, the YAG:Ce^{3+} powders show large grains with smooth surfaces but became very rough after $MAPbBr_{2.5}I_{0.5}$ coated on them.

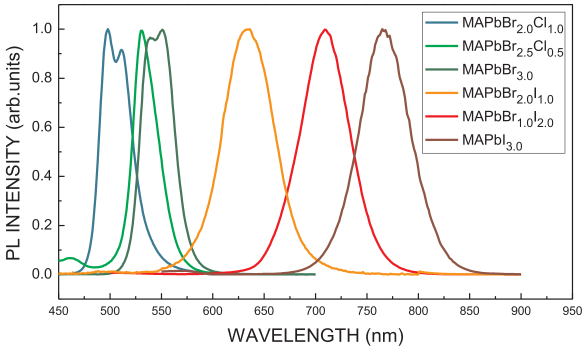

Fig. 3. PL spectra of various perovskite powders.

Fig. 6(a) shows the X-ray diffraction (XRD) pattern of the YAG:Ce^{3+} powders (red curve), $MAPbBr_{2.5}I_{0.5}$ powders (red curve), and $MAPbBr_{2.5}I_{0.5}$ coated YAG:Ce^{3+} powders (black curve). A very weak (100) peak of $MAPbBr_{2.5}I_{0.5}$ cubic phase located at 14.8° was found, as shown in Fig. 6(b), which means that the $MAPbBr_{2.5}I_{0.5}$ crystal grew on the surface of YAG:Ce^{3+} and had small grain sizes or thin thickness. Indeed, the SEM images show that the $MAPbBr_{2.5}I_{0.5}$ species is highly dispersed on the YAG:Ce^{3+} surface, as shown in Fig. 6(b).

Table 1 summarizes PL quantum efficiency (PLQE) for YAG:Ce3+ and perovskite-coated powders. Pure perovskite powders cannot be detected by our system due to weak PL intensity. The YAG:Ce3^{+} powder show the best quantum efficiency. After perovskite coating, the decrease in quantum efficiency and the increase in absorbance can be seen. This indicates the PL efficiency of the perovskite materials need to be improved in the future work. Several method can be used to increase the PL efficiency of the perovskite materials, like perovskite quantum dots [20].

Fig. 7 displays the structure of warm white LED with remote perovskite-coated YAG phosphor films. The phosphor layers were fabricated using 30 mg YAG and 50 mg perovskite-coated powders added in 1 ml PDMS. Fig. 8 shows photos of blue LED with YAG:Ce^{3+} and $MAPbBr_{3-x}I_x$-coated YAG:Ce^{3+}. The operating voltage was set at 10 V. The emitting color reveals very uniform and can be distinguish by naked eye.

Fig. 9 shows the electroluminescence (EL) spectrum of the white LED formed by blue LED (450 nm; LiteOn Corp.) with YAG:Ce^{3+} and $MAPbBr_{3-x}I_x$-coated YAG:Ce^{3+}. The spectrum of YAG:Ce^{3+} sample includes two peaks located at 450 and 560 nm. The 450 nm peak is contributed by blue LED as excitation light source. The 560 nm peak is a broad band which is emitting from luminescent of lanthanide ions Ce^{3+}. After perovskite coated, new broad bands appear. The corresponding locations of $MAPbBr_{2.5}I_{0.5}$ and $MAPbBr_{2.0}I_{1.0}$ are 600 and 620 nm, respectively, which have more red light contribution than YAG:Ce^{3+} sample. The chromaticity coordinate of YAG:Ce^{3+} sample was (x = 0.3134, y = 0.3497). However, those of $MAPbBr_{2.5}I_{0.5}$ and

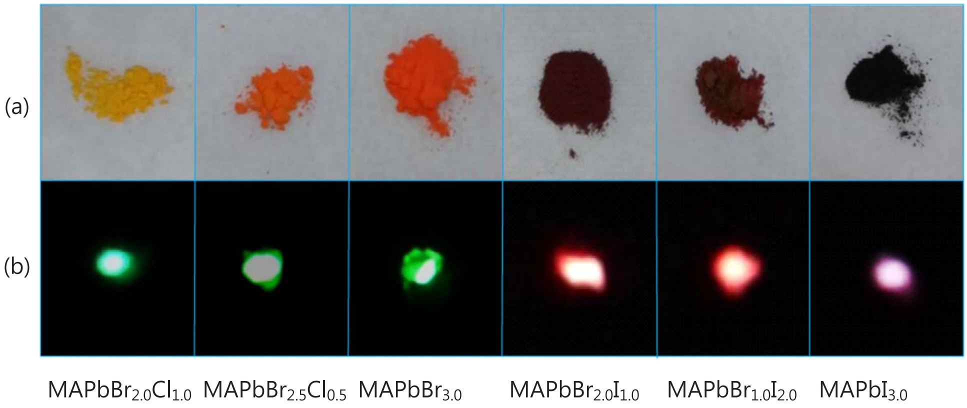

Fig. 2. (a) Photographic and (b) photoluminescence images of perovskite $MAPbX_3$ powders with various ratios of Cl, Br, and I.