Original Article

Synthesis and Waterproofness Improvement of K₃AlF₆:Mn⁴⁺ Phosphor for Warm White Light-emitting Diodes

Le Quoc Dat, Duong Thanh Tung, Nguyen Duy Hung*  

Advanced Institute for Science and Technology, Hanoi University of Science and Technology, 1 Dai Co Viet, Hai Ba Trung, Hanoi, Vietnam

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Abstract: In this study, we synthesized K₃AlF₆:Mn⁴⁺ phosphor by co-precipitation method and investigated its crystal structure and photoluminescence properties. By surface modification of K₃AlF₆:Mn⁴⁺ using K₃AlF₆, the moisture resistance performance of the phosphor can be significantly improved. It was found that the luminescence performance of K₃AlF₆:Mn⁴⁺@K₃AlF₆, which was dispersed in water for 2 h, was unchanged but the uncoated sample reduced dramatically. White light emitting diodes (WLEDs) based on the phosphor combined with commercial YAG:Ce³⁺ coated on a blue LED showed significant improvement of performance with color correlated temperature (CCT) from 5307 K down to 3528 K and color rendering index (CRI) from 64 up to 87. The results exhibit the potential for the application of K₃AlF₆:Mn⁴⁺@K₃AlF₆ as a red phosphor in warm WLEDs.

Keywords: K₃AlF₆:Mn⁴⁺, phosphor, optical properties, surface modification, moisture resistance, warm WLED

1. Introduction

The commercialized WLEDs have based on combination of blue-emitting InGaN chip with a yellow phosphor (YAG:Ce³⁺). The WLEDs have a good luminous efficiency but a poor CRI and a CCT because of the lack of red emission [1-3]. To improve the two color parameters of the WLED, red phosphors need to be combined to the WLED [4-6]. Among the various red phosphors, Eu²⁺-doped nitrides have been reported as a good class of phosphors for WLEDs. However, the production cost is expensive due to the rigorous condition synthesis and high cost of the raw materials [7]. Recently, non-rare-earth ion
activated phosphors have been an important material in developing WLED because these raw materials are cheaper than rare-earth doped nitride materials, and they can exhibit red light under the excitation of blue light. Red phosphors doped with transitional metal Mn\(^{4+}\) ions were widely studied for LED-based devices. Mn\(^{4+}\)-activated oxide-based red phosphors have broad absorption bands in the range of 300-500 nm and produce intense red emissions in the 600-700 nm wavelength range, and so, they have been more thermally stable and environmentally friendly [8-11]. The Mn\(^{4+}\)-activated oxide-based red phosphor has a low blue region absorption efficiency which is a drawback of the phosphor. Recently, Mn\(^{4+}\)-doped fluorides were widely developed for WLEDs due to their sharp red emissions around 630 nm under blue excitation, but they inherit poor moisture resistance due to their instability [8, 12]. To improve the stability of Mn\(^{4+}\)-doped fluorides, a coating layer on the phosphor surface for bettering the moisture resistance. Some authors reported a moisture-resistant Mn\(^{4+}\)-doped fluoride phosphor with host lattice material, alkyl phosphate, hydrophobic oleic acid, alkyl trimethoxy-silane, DL-mandelic acid, SiO\(_2\), Al\(_2\)O\(_3\), InO\(_2\), CaF\(_2\),… [13-19]. K\(_3\)AlF\(_6\):Mn\(^{4+}\) has been reported as a better thermal, chemical stability, melting point and lower water solubility than K\(_2\)SiF\(_6\) [20-23]. Red emitting phosphor K\(_3\)AlF\(_6\):Mn\(^{4+}\) presented excellent luminescence performances [24, 25]. However, the phosphor suffers from luminescence degradation in high moisture environment. Thus, K\(_3\)AlF\(_6\):Mn\(^{4+}\) phosphor needs to be coated to enhance moisture resistance.

In this paper, we report on a red emitting K\(_3\)AlF\(_6\):Mn\(^{4+}\) phosphor synthesized by co-precipitation method. It is found that K\(_3\)AlF\(_6\):Mn\(^{4+}\) phosphor is extremely sensitive to humidity. The K\(_3\)AlF\(_6\):Mn\(^{4+}\)crystal surface treated by a The K\(_3\)AlF\(_6\):Mn\(^{4+}\)@K\(_3\)AlF\(_6\) proves an improved stability under water immersion. By employing the red phosphor, we fabricated warm WLEDs with a low CCT and a high CRI.

2. Experiment

2.1. Sample Preparation of K\(_3\)AlF\(_6\):Mn\(^{4+}\)

K\(_3\)MnF\(_6\) was synthesized according to the method described in the literature [26]. Specifically, 0.1 g KMnO\(_4\) and 2 g KF were completely dissolved in 9 ml HF (40%) solution with a plastic beaker. The mixed solution was cooled to -30 °C for 48 h. Then H\(_2\)O\(_2\) solution was added drop by drop until the solution turned yellow. The yellow powder of K\(_3\)MnF\(_6\) sample was obtained by filtering, washing with acetone and drying at 60 °C for 5 h.

K\(_3\)AlF\(_6\) was synthesized via a room temperature coprecipitation method using DI water as the solvent. In a typical synthesis: First, 12 mmol of Al(NO\(_3\))\(_3\)9H\(_2\)O was dissolved in 55 mL H\(_2\)O and 222 mmol of KF was dissolved in 45 mL H\(_2\)O. The solutions were mixed together and stirred for 30 min to form uniform mixture. Then the solution was kept at 25 °C for 24 h to form precipitate. Finally, the precipitate was collected by centrifugation, washed several times with absolute ethanol and deionized water and dried at 80 °C for 4 h to get K\(_3\)AlF\(_6\) powder.

For synthesis of K\(_3\)AlF\(_6\):Mn\(^{4+}\) red phosphor, in a typical synthesis of Mn4+-doped sample, 0.6 mmol K2MnF6 was dissolved in 8 ml HF (40%) solution into a plastic beaker. 12 mmol of K\(_3\)AlF\(_6\) was added into the beaker and completely dissolved with stirring. Then the reaction mixture was kept at various temperature from -10 °C to 80 °C for 2 h. The precipitate was collected by centrifugation, washed several times with absolute ethanol and deionized water to remove eventual soluble contaminants. Then the solution was dried at 80 °C for 12 h to obtain the final productions.

2.2. Surface Passivation of K\(_3\)AlF\(_6\):Mn\(^{4+}\)
The surface modification of K$_3$AlF$_6$:Mn$^{4+}$ was performed by using K$_3$AlF$_6$ solution. The K$_3$AlF$_6$:Mn$^{4+}$ powder was dispersed in the K$_3$AlF$_6$ solution and stirred for 30 min. The K$_3$AlF$_6$:Mn$^{4+}$@K$_3$AlF$_6$ was collected by centrifugation and dried at 80 °C for 5 h.

2.3. Analytical Methods

Crystal structure of K$_3$AlF$_6$:Mn$^{4+}$ sample was characterized by powder x-ray diffraction (XRD) on a Siemens D5005 diffractometer equipped with a CuKα radiation source (λ = 1.5406Å). Morphology of the product was investigated by field emission scanning electron microscopy (FESEM, JSM-7600F, Jeol, Japan) at an acceleration voltage of 15 kV. Excitation and emission spectra were measured on a fluorescence spectrophotometer (NanoLog, Horiba, USA) equipped with a 450 W xenon discharge lamp as an excitation source at room temperature. The photoelectronic properties of the LED devices were recorded using an integrating sphere coupled to a spectrofluorometer (Gamma Scientific, USA).

3. Results and Discussion

Figure 1 shows the XRD patterns of the as-synthesized samples K$_3$AlF$_6$:Mn$^{4+}$. All the observed diffraction peaks well-indexed to α-K$_3$AlF$_6$ with tetragonal superstructure (PDF#00-057-0227). The cell parameters of α-K$_3$AlF$_6$ are $a = 18.8385(3)$ Å, $b = 18.8388(5)$ Å, $c =33.9657(6)$ Å, $\gamma = 90^\circ$, $V = 12053.6(3)$ Å$^3$, and $Z = 80$. No impurity crystal phases are observed, which confirms that the phosphor sample is single phase.

![Figure 1. XRD patterns of K$_3$AlF$_6$:Mn$^{4+}$ synthesized by co-precipitation method.](image)

The emission spectrum consists of several sharp emission peaks at around ~626 nm, corresponding to the spin-forbidden $^2$Eg $\rightarrow$ $^4$A$_2$ transitions of Mn$^{4+}$. That is, emission peaks at 596, 605, 610, 618, 626.5, 630.5, and 643.5 nm are attributed to the anti-Stokes $\nu_3(t_{1u})$, $\nu_4(t_{1u})$, and $\nu_6(t_{2u})$, zero phonon line (ZPL), Stokes $\nu_6(t_{2u})$, $\nu_4(t_{1u})$, and $\nu_3(t_{1u})$ vibronic modes, respectively [24, 25]. In this work, the ZPL peak is stronger compared to previously observed Mn$^{4+}$ activated fluoride such as K$_3$(Si,Ge,Ti)F$_6$ due to the relatively lower symmetry of the substituted distorted octahedral Al$^{3+}$ site in α-K$_3$AlF$_6$ [27]. The excitation spectrum (monitored at 626 nm) contains two broad excitation bands centered at ~360 and ~460 nm, originating from the spin allowed $^4$A$_2$ $\rightarrow$ $^4$T$_1$ and $^4$A$_2$ $\rightarrow$ $^4$T$_2$ transitions of Mn$^{4+}$, respectively. Notably, the blue excitation band (~460 nm) is much stronger than the ultraviolet (UV) (~360 nm) excitation band, and almost no spectral overlap can be observed between the emission spectrum of the
commercial yellow phosphor YAG:Ce³⁺ and the excitation spectrum of α-K₃AlF₆:Mn⁴⁺, indicating that the common problem of reabsorption can be resolved by using this present phosphor for the red light component.

Figure 2. PLE (a) and PL (b) spectra of K₃AlF₆:Mn⁴⁺ phosphor measured at room temperature.

The influence of reaction temperature on luminescence intensity of K₃AlF₆:Mn⁴⁺ is described in Figure 3. The PL spectrum has the same shape and peak when reaction temperature changes from -10 °C to 80 °C. It is obvious that the emission intensity of the phosphor increases with the reaction temperature, until it reaches 30 °C, which is probably due to the improved crystallization. However, with the further increase in reaction temperature, the emission intensity decreases. This might be because Mn⁴⁺ tends to oxidize to non-emission Mn³⁺ at higher temperature. To confirm the moisture resistance of prepared K₃AlF₆:Mn⁴⁺ and K₃AlF₆:Mn⁴⁺@K₃AlF₆, the water immersion testing was performed for 2 h. It is clearly seen that there is no change in the shape of PL spectra of the phosphors. However, PL intensity of K₃AlF₆:Mn⁴⁺ reduces quickly to 8%, while K₃AlF₆:Mn⁴⁺@K₃AlF₆ maintains about 91% of initial intensity after 2 hours’ water immersion. This result illustrates that the K₃AlF₆ shell is the main reason to improve the moisture resistance.

Figure 3. PL spectra (a) and PL intensity (b) of the phosphors were synthesized at various temperature.

Finally, the red phosphor is packed with yellow phosphor YAG:Ce³⁺ and blue chip to assess the performance of application in warm WLED devices. Figure 5a shows the electroluminescent (EL)
spectra of the devices based on blue chip LEDs coated YAG:Ce$^{3+}$ and the red phosphor mixture under 150 mA current excitation. The peak at ~ 460 nm is attributed to the emission of LED chip and the broadband emission in yellow light peaking at around 550 nm is due to YAG:Ce$^{3+}$ phosphor while the peaks at 626 nm are due to the emission of $K_3\text{AlF}_6$:Mn$^{4+}$@$K_3\text{AlF}_6$ phosphor. As the amount of $K_3\text{AlF}_6$:Mn$^{4+}$@$K_3\text{AlF}_6$ increases, the electroluminescence spectra of the WLEDs show an increased red component. The chromaticity coordinates of the five typical WLEDs were close to the black body radiation locus, as marked in Figure 5b.

![Figure 4](image1.png)

Figure 4. PL spectra of $K_3\text{AlF}_6$:Mn$^{4+}$ (a), $K_3\text{AlF}_6$:Mn$^{4+}$@$K_3\text{AlF}_6$ (b) and PL intensity as function of water immersing times of $K_3\text{AlF}_6$:Mn$^{4+}$ (c), $K_3\text{AlF}_6$:Mn$^{4+}$@$K_3\text{AlF}_6$ (d)

CCT of WLED reduces from 5307 to 3528 and CRI increases from 64 to 87 when mass ratio of YAG:Ce$^{3+}$ and $K_3\text{AlF}_6$:Mn$^{4+}$ changes from 1:1 to 1:4. To further evaluate the performance of the warm WLEDs, the device with the lowest CCT and highest CRI are chosen to record electroluminescence spectra under different drive currents between 50 and 350 mA and temperatures from 15 °C to 105 °C. It is observed that the shape of electroluminescence spectra is changed significantly with three contributed emission bands from the chip and the two typical phosphors. When the drive current and temperature of the device increase, the warm WLED only produces very small fluctuations in CCT and CRI. The above electroluminescent results demonstrate that $K_3\text{AlF}_6$:Mn$^{4+}$@$K_3\text{AlF}_6$ may serve as a red emitting phosphor for warm WLEDs.
4. Conclusion

In this study, $K_3\text{AlF}_6:\text{Mn}^{4+}$ phosphor was prepared by co-precipitation method. The $K_3\text{AlF}_6:\text{Mn}^{4+}$ phosphor emitted intense red light with sharp line in 590 – 650 nm region and presented broadband excitation in blue light, matching well with blue LED chips. By coating $K_3\text{AlF}_6$ on $K_3\text{AlF}_6:\text{Mn}^{4+}$, the moisture resistance of the phosphor was improved. The warm WLED was fabricated by the combination of YAG:Ce$^{3+}$ yellow, $K_3\text{AlF}_6:\text{Mn}^{4+}@K_3\text{AlF}_6$ red phosphor and blue LED chip. The results indicate that the red phosphor may be promising red phosphor for warm WLED.

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References


