Effects of Fe²⁺ on Moisture Resistance of Fluoride Red Phosphors

CAI Wenting^{1,2, a}

¹Jiangxi University of Science and Technology

² Key Laboratory of Rare Earth Luminescence Materials and Devices of Jiangxi Province, Faculty of Materials Metallurgy and Chemistry

Abstract. Nowadays, K₂SiF₆:Mn⁴⁺ has been made extensive use of in technologies available, applied to LCD (Liquid crystal display) and pc-WLEDs (Phosphor-converted white light-emitting diodes). Nevertheless, there are still some significant problems needing solved, one of which is the poor moisture resistance. To expand its application in optical devices, this paper proposes a green and simple strategy on the basis of Fe²⁺, which effectively achieves a reduction of the reaction between water and luminescence center.

1 Introduction

It's universally acknowledged that phosphor-converted white light-emitting diodes (pc-WLEDs) are green, environmentally friendly and long-lived. Phosphors play a significant role in colour gamut (CG), lumen efficiency, correlated colour temperature (CCT) and colour-rendering index (CRI) of pc-WLEDs. Nevertheless, the bad moisture resistance is an evidently important challenge, which limits its application in further market^[1-3].

Nowadays, the general methods for improving the moisture resistance of water-vapor-sensitive optical materials can be divided into two categories according to the formation of the water-resistant layer. One is to coat an organic or inorganic hydrophobic isolation layer on the surface of the material for the purpose of reducing active ions or exposure of reactive groups. Based on this method, the strategy of isolating the luminescent center [MnF₆]²⁻ group of the Mn⁴⁺-doped fluoride red phosphor from the external moisture environment came into being. Numerous hydrophobic organic coating materials such as alkyl phosphate and octadecane Trimethoxysilane, DL-mandelic acid, oleic acid and inorganic coating materials such as CaF₂, Al₂O₃, TiO₂ and nano-scale carbon (C) layers have been developed to be painted on the surface of phosphor particles, which enhances the moisture resistance of the Mn⁴⁺-doped fluoride red phosphor. Although the surface coating can effectively improve the moisture resistance of the Mn⁴⁺-doped fluoride red phosphor, due to the uneven and incomplete deposition of the coating material, the partial area of the phosphor particles cannot be fully covered yet, which brings about moisture erosion^[4]. In addition, on account of the poor light transmittance of the coating material, the luminous efficiency of Mn⁴⁺ doped fluoride

phosphors is evidently reduced after modified coating. Therefore, applying organic or inorganic coatings on the surface of Mn⁴⁺-doped fluoride phosphor particles cannot solve the problem of poor moisture resistance. The other is to form a hydrophobic protective layer in situ on the surface of the material. It has been reported that H₂O₂ or oxalic acid solution is used to improve the water resistance of fluoride red phosphors, and there are fewer reagents available^[5]. Hence, in order to solve the poor moisture resistance of Mn⁴⁺-doped fluoride red phosphors perfectly, new modification reagents still need to be further developed^[6].

Accordingly, this paper puts forward a proposal on the basis of Fe²⁺ reduction, which assists K₂MnF₆:Mn⁴⁺ red phosphor particles attaining immense moisture resistance.

2 Experiment

2.1 Preparation of K₂SiF₆:Mn⁴⁺

In this experiment, the raw materials are 40% HF (analytical purity), KF (analytical purity), and SiO₂ (analytical purity). To begin with, attain the precursor of K₂MnF₆. Then, according to the stoichiometric ratio, weigh the raw materials, dissolve 7.034 g of SiO₂ in a beaker containing 150 ml of HF and stir well, add 2.693 g of K₂MnF₆ and mix them to form the mother liquor. Next, dissolve 21.0358 g KF in 100 mL of HF, and after the form of transparent solution, pour it into the mother liquor. Ultimately, precipitate, wash, and dry, so attain KSF powder.

^a Corresponding author: 1320181521@mail.jxust.edu.cn

2.2 KSF's control experiment

Weigh 1.002 g of untreated KSF samples into two test tubes, add 20 mL of 0.5 mol/L FeCl_2 solutions, getting the T-KSF. Weigh 4.859 g of potassium thiocyanide, dissolve it in deionized water, transfer it into a 500 mL volumetric flask, dilute to the mark with deionized water, shake well and prepare it for immediate use. Measure 20 mL of FeCl_2 into two test tubes, named test tube A and test tube B. Add 1 g of KSF to test tube A, which is as a proof of Fe^{2+} reduction 55^{2-} , while test tube B as a blank control, and use 10 mL of 0.1 mol/L KSCN to titrate to the end point.

2.3 KSF post-processing

Pipette 0.2 L of 0.5 mol/L FeCl_2 solution into a beaker containing 10.003 g of the KSF sample prepared above, stir for 12 h, and collect by centrifugation at 2500 r/min.

2.4 LED package

To study the use of processed T-KSF phosphors in WLEDs performance, T-KSF phosphor is used as the red component, mixed with yellow commercial phosphor $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG: Ce^{3+}) and epoxy resin, and then packaged them with blue chips InGaN.

2.5 Sample characterization

The sample was characterized by a BRUKER D8ADVANCED X-ray powder diffractometer. The radiation source was $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$), the morphology of the sample was characterized by scanning electron microscope (SEM, TM3030), the particle surface distribution of the sample was characterized by energy spectrum (EDS) for characterization. The photoluminescence excitation spectrum (PLE) and photoluminescence spectrum (PL) were measured by using a Hitachi F-7000 fluorescence spectrometer equipped with a 450 W xenon lamp. The

fluorescence lifetime was measured with FLS920 (Edinburgh) spectrometer. The variable temperature emission spectrum was detected by a thermal quenching analysis system (EX-1000, Everfine, China). Quantum efficiency (QE) was measured by a Hitachi F-7000 fluorescence spectrometer with using the method of Ba_2SO_4 wrapping the integrating sphere. X-ray photoelectron spectroscopy (XPS) spectroscopy was detected by scanning XPS microprobe system (Phi5000 versaprobs-ii, Ulvac-Phi). The performance of LEDs was measured by using an integrating sphere spectroradiometer system (HAAS-2000, Everfine, China).

3 Results and discussion

3.1 Analysis of morphology and surface composition of KSF and T-KSF samples

Figure 1 (a) and (b) are the SEM images of KSF and T-KSF, respectively. It can be seen from the comparison that the KSF sample exhibits a slight agglomeration phenomenon, while the degree of aggregation of the T-KSF sample particles after the FeCl_2 solution treatment is effectively reduced, and the dispersibility of the phosphor particles is significantly improved, resulting in enhancing luminous efficiency. The treatment of FeCl_2 solution has no obvious effect on the particle size, and the particle size before and after the treatment is approximately 4-10 μm . It is worth mentioning that the surface of the KSF sample particles is relatively smooth, and the surface smoothness of the T-KSF powder is significantly reduced, indicating that the surface of the T-KSF particles has no Mn^{4+} doped matrix protective shell successfully formed.

Figure 1 (c) and (d) are the EDS mapping image spectra of KSF and T-KSF, with the K, Si, F, Mn element mappings of KSF and T-KSF samples, respectively. It can be seen from the figure that the KSF and T-KSF

Fig.1 SEM images of KSF (a) and T-KSF (b). EDS mapping images (c) and K, Si, F, Mn elemental mapping images of KSF. EDS mapping images and K, Si, F, Mn elemental mapping images of T-KSF.

samples have detected obvious signals corresponding to the F, K, Si, and Mn elements, and the distribution is relatively uniform. In particular, the treatment of FeCl_2 solution makes the Mn signal detected on the surface of T-KSF phosphor particles significantly lower than that of KSF, in other word, the Mn content on the surface of T-KSF particles is lower than that of KSF, which is mainly because the treatment with FeCl_2 solution makes the particle surface uniform and almost free of Mn protective shell K_2SiF_6 . In order to further study the surface composition of the T-KSF sample particles, we used XPS (a solid surface chemical composition analysis technique that can be used to detect the depth of 10 nm) to detect the Mn element on the surface of the KSF and T-KSF samples, and found KSF has more Mn content and higher distribution density, while T-KSF had less Mn content.

3.2 Electroluminescence characteristics of T-KSF

In order to study the practical application prospect of T-KSF red phosphor, WLED was made by packaging T-

KSF red phosphor, YAG: Ce^{3+} yellow phosphor and blue InGaN chip. Figure 2(a) is the electroluminescence (EL) spectrum of the WLED device after packaging and the image of the WLED before and after power-on. As shown in the figure, under the driving current, the WLED emits bright warm white light, and the addition of phosphor T-KSF significantly enhances the red light emission of the WLED device, which makes the light colour quality of the WLED significantly improved. Figure 2(b) is the CIE chromaticity diagram of the packaged WLED device under the excitation of 460 nm blue light. The colour coordinates of the WLED device are (0.4110, 0.3963), which is in the warm white light region. It shows that the T-KSF obtained after Fe^{2+} treatment has the development potential of being used as a red lighting component in the LEDs lighting market.

Figure 2(c) shows the electroluminescence spectra of WLED devices under different driving currents after packaging. The spectrum shows that the shape of the electroluminescence spectrum of the WLED device remains basically unchanged with the increase of the driving current, the colour fluctuation is small, and the emission spectrum line only shows a weak red shift.

Fig.2 (a) EL spectra of WLED, the inset displays the camera photos of the light and lightless WLED devices. (b) The corresponding CIE chromaticity diagram. Under various drive currents, WLED's (c) electroluminescent spectra and (d) Ra.

Figure3(d) is a histogram of the colour rendering index changes of WLED devices under different driving currents after packaging. The colour rendering index of WLED at 20 mA is 81.6, which is a warm white fluorescent emission, indicating that the doping of T-KSF effectively improves the colour rendering performance of WLED devices. It is worth noting that the display index (Ra) only fluctuates by 0.61% under the driving current of 20-300 mA, indicating that the display index of WLED is less affected by the driving current and has relatively high colour stability. As the current increases, the lumen efficiency of WLEDs slowly decreases, and the correlated colour temperature rises rapidly. It shows that the doping of T-KSF red phosphor can effectively optimize the colour temperature to obtain a warm white light device with a correlated colour temperature (CCT) less than 3500 K. It can be seen that by balancing the lumen efficiency and correlated colour temperature parameters, WLEDs with different luminous effects can be produced. Therefore, the drive current can be adjusted to make the WLED device suitable for different lighting occasions.

In summary, through the oxidation and reduction of Fe^{2+} ions, T-KSF can be obtained with high luminous intensity, high humidity resistance and high thermal stability. By adding appropriate T-KSF red phosphors to the LED device, warm WLED devices with high colour rendering index, low colour temperature and low colour temperature can be attained for being used in the lighting market.

4 Conclusion

Ultimately, for the sake of attaining T-KSF phosphor, $\text{K}_2\text{SiF}_6\text{:Mn}^{4+}$ red phosphor is synthesized by using co-precipitation method and post-processed with FeCl_2 . After FeCl_2 solution treatment, the thermal stability, moisture resistance and luminous intensity of T-KSF are evidently higher than that of KSF. Under 20 mA drive current, the T-KSF packaged WLED emits warm white light, its colour coordinates locate in the red region (0.4110, 0.3963), the correlated colour temperature (CCT) is less than 3500 K, and the colour rendering index is 81.6 Hence, this work provides a green and simple redox strategy for Fe^{2+} ions to improve the moisture resistance of fluoride red phosphors for new high-efficiency WLEDs.

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