Highly Stable Mn^{4+} -Activated Red-Emitting Fluoride Phosphors and Enhanced moisture stability for White LEDs

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Abstract. As a highly productive narrow-band emission red phosphor, $\text{K}_2\text{SiF}_6\text{:Mn}^{4+}$ has towardly application market in pc-WLEDs (Phosphor-converted white light-emitting diodes) and LCD (Liquid crystal display). However, the poor moisture resistance property is recognized impediment for generalizing its wider commercialization. Herein, we adopt a simply green and convenient strategy based on Fe^{2+} , which is committed to decreasing the reaction between luminescence center and water. The $\text{K}_2\text{SiF}_6\text{:Mn}^{4+}$ as expected exhibits highly efficient red emission upon excitation.

1 Introduction

Phosphor-converted white light-emitting diodes (pc-WLEDs) are considered as a new generation of green lighting sources. On account of its excellent properties such as energy saving, long service life, and environmental protection, it is universally acknowledged that it's used in indoor and outdoor lighting and liquid crystal display (LCD) backlight sources^[1-4]. Phosphors, as one of the core materials of pc-WLEDs, play a significant role on the color-rendering index (CRI), correlated color temperature (CCT), and lumen efficiency of pc-WLEDs (Luminous efficiency, LE) and other optical quality parameters^[5-8]. The current chemical formula is $\text{A}_3\text{YF}_6\text{:Mn}^{4+}$ (A is alkali metal or alkaline earth metal element; $\text{X}=\text{Si}^{4+}$, Ge^{4+} and Ti^{4+} , etc.) and $\text{A}_2\text{YF}_6\text{:Mn}^{4+}$ ($\text{Y}=\text{Al}^{3+}$, Ga^{3+} and Sc^{3+} , etc.) Mn^{4+} activated fluoride red phosphor, which has the advantages of high luminous efficiency, high color purity, main emission peak (~ 630 nm) located in the visible light sensitive region of the human eye, and blue light region (~ 450 nm) broadband absorption, etc.^[9-18] Therefore, it is well-known that it's the most promising new generation of red phosphor^[18-24]. It is one of the current research hotspots in the field of red phosphor research. However, due to the inherent moisture resistance of this type of fluoride red phosphors, the service life and light color quality of pc-WLEDs in practical applications have suffered huge challenges^[24-30].

Consequently, this paper proposes a strategy based on Fe^{2+} ion reduction, which realizes the in-situ generation of Mn-free KSF on the surface of $\text{K}_2\text{SiF}_6\text{:Mn}^{4+}$ red phosphor particles, and obtains T-KSF phosphor with excellent moisture resistance.

2 Experiment

The raw materials used in this experiment are SiO_2 (analytical purity), KF (analytical purity), and 40% HF (analytical purity). First, obtain the precursor of K_2MnF_6 . Weigh the raw materials according to the stoichiometric ratio, dissolve 7 g of SiO_2 in a beaker containing 150 ml of HF and stir well, then add 2.693 g of K_2MnF_6 and mix to form a mother liquor. Next, dissolve 21 g KF in 100 mL of HF, and when a transparent solution was formed, pour it into the mother liquor. Finally, precipitated, washed, and dried to obtain KSF powder.

Weigh 1 g of untreated KSF samples into two test tubes, add 20 mL of 0.5 mol/L FeCl_2 and HCl solutions respectively. Consequently, obtain T-KSF and P-KSF phosphors respectively after 12 hours of treatment, which helps to eliminate the effect and interference of Cl^- in the solution.

Pipette 200 mL of 0.5 mol/L FeCl_2 solution into a beaker containing 10 g of the KSF sample prepared above, stir for 12 h, and collect by centrifugation at 2500 r/min. The product was washed twice with acetic acid and ethanol, and then dried in an oven at 60 °C for 4 hours to prepare T-KSF phosphor.

Weigh 1 g of KSF and treated T-KSF phosphors in 20 mL of deionized water for immersion treatment, and treat them in a test tube for 1 min, 5 min, 10 min, 20 min, 40 min, 80 min, and 160 min, 240 min and 320 min, so that obtain a series of materials with different immersion time.

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3 Results and discussion

3.1. Luminescence performance

In order to study on the luminescence performance of T-KSF after Fe^{2+} solution treatment, 0.5 mol/L FeCl_2 solution was prepared through experiments, which used for the post-treatment of KSF samples. Figure 1 shows the PLE and PL spectra of T-KSF and KSF. The near-ultraviolet excitation peak at about 360 nm and the blue excitation peak at about 468 nm can be observed in the PLE spectra. They are derived from Mn^{4+} and in the transitions of ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$. The strongest excitation peak is located in the blue region, which can be well matched with the blue chip. Under the blue light's excitation of 468 nm, the strongest narrow-band emission peak of the sample is located at 632 nm, coming from the parity forbidden and spin forbidden transition of Mn^{4+} from the low excited state ${}^2\text{E}_2(\text{t}_2^3)$ energy level to the ground state ${}^4\text{A}_2(\text{t}_2^3)$ energy level, which is sensitively visible light by the human eye. By comparing the spectra of T-KSF and KSF, it can be found that, except for the luminous intensity, there is no obvious difference in the shape and peak position of the excitation and emission spectra of T-KSF and KSF samples, which indicates that Fe^{2+} ions did not change the crystal structure of KSF while improving the luminescence performance of the phosphor. In addition, the luminescence intensity of the T-KSF sample is significantly higher than that of KSF, for it is a protective shell formed on the surface of the T-KSF phosphor particles after the FeCl_2 solution treatment, which effectively reduces the probability of non-radiative transition of Mn.

Fig.1 The excitation and emission spectrum of KSF and none, respectively.

3.2 Decay curves

Figure 2 shows the fluorescence decay curves of KSF and T-KSF. Fitting shows that the fluorescence decay of KSF and T-KSF samples conforms to the first-order exponential decay mode, and the formula is as follows:

$$\tau = \frac{\int_0^{\infty} tI(t) dt}{\int_0^{\infty} I(t) dt}$$

Among them, $I(t)$ is the fluorescence intensity of the sample at time t . After fitting, the fluorescence lifetimes of T-KSF and KSF are 6.35 ms and 6.33 ms, respectively. The reason why the fluorescence lifetime of T-KSF is higher than that of KSF is that after FeCl_2 solution treatment, the content of Mn in T-KSF is significantly lower than that of KSF, which shows that the T-KSF sample obtained after FeCl_2 solution treatment still has good luminous performance.

Fig.2 The decay curves of KSF and T-KSF's

3.3 Thermal stability

In applications, since the temperature of the LED chip will increase during operation, phosphor, which is one of the constituent materials of WLEDs, its thermal stability has a significant impact on the light efficiency, light color quality and stability of WLEDs. In order to study on the thermal stability of T-KSF samples treated with FeCl_2 solution, Figure 3 shows the relative luminous intensity of KSF and T-KSF phosphors in the temperature range of 298 to 473 K. The relative luminous intensity of KSF and T-KSF phosphors varies with temperature and it can be seen from the figure that the trends of KSF and T-KSF are consistent. When the temperature is between 298 and 323 K, the luminous intensity of KSF and T-KSF slowly increases with the increase of temperature, and the reason for the enhancement may be that after the redox reaction, the Fe^{2+} and Mn^{4+} on the surface decrease, which leads to the decrease of the fluorescence quenching center. Then in the temperature range of 323 ~ 473 K, the luminous intensity of two shows a gradual decrease trend at the same time. This is mainly due to the high temperature intensifying the lattice vibration of the phosphor, which contributes to the enhancement of the luminescent center's lattice relaxation and no radiation. Meanwhile, the probability of transition increases, which ultimately reduces the luminous efficiency of the sample. In addition, as the temperature rises, the crystal structure of the phosphor surface increasingly gets destroyed, more and more Mn^{4+} becomes oxidized, which makes the phosphor luminescent center or the surrounding matrix

lattice undergo essential changes, resulting in a substantial decrease in the luminous intensity of the sample.

Fig.3 The temperature dependence photoluminescence intensity of KSF and T-KSF's

3.4 Moisture stability

Figure 4 indicates the relative luminous intensity changes of KSF and T-KSF phosphors under different soaking times. With the extension of water immersion time, due to the inherent poor moisture resistance of fluoride red phosphor, the relative luminous intensity curves of T-KSF and KSF samples decline at different rates, but the decline rate of T-KSF is significantly slower. After 320 minutes of soaking, the relative luminous intensity of the KSF phosphors dropped drastically, which was only 63.4% of the initial intensity value, while the T-KSF sample still maintained 80.3% of its original intensity. Above all, it indicates that the moisture resistance of T-KSF samples is always better than that of KSF samples without Fe^{2+} treatment under different immersion times, which means that the moisture resistance of KSF samples has been significantly improved after FeCl_2 solution treatment. The reason why the moisture resistance of T-KSF samples is improved is that the successful treatment of FeCl_2 solution forms a protective shell without Mn^{4+} doping on the surface of the original KSF particles, which has a self-protection effect on the T-KSF particles and effectively reduces the luminescent center ion inside the T-KSF particles in direct contacting with water. To conclude, it makes T-KSF samples less prone to hydrolysis in long-term using in air or humid environments, which is conducive to the long-term use of WLEDs.

Fig.4 The photoluminescence intensity in different immersed time of KSF and T-KSF's

4 Conclusion

In this paper, a co-precipitation method was used to synthesize $\text{K}_2\text{SiF}_6:\text{Mn}^{4+}$ red phosphor, and post-processed with FeCl_2 to obtain T-KSF phosphor. The particle size distribution of this series of samples is approximately 4-10 μm . Under the excitation of 468 nm blue light, this series of samples has a strongest narrowband emission peak at 632 nm in the range of 550-700 nm. The luminous intensity, moisture resistance and thermal stability of T-KSF after FeCl_2 solution treatment are significantly higher than that of KSF, and the fluorescence lifetime is 6.35 ms. Under 20 mA drive current, the T-KSF packaged WLED emits warm white light, its color coordinates are in the red region (0.4110, 0.3963), the color rendering index is 81.6, and the correlated color temperature (CCT) is less than 3500 K. Therefore, 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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