Preparation and Luminescence Properties of K$_2$MgSiO$_4$:Mn$^{4+}$ Phosphor

Dai Chen, Zhisen Li, Yan Wen, Shiqing Man*

School of Physics and Electronic Information, Yunnan Normal University, Kunming, Yunnan, 650500, China

*Corresponding author: sqman_ynnu@ynnu.edu.cn

Abstract. The K$_2$MgSiO$_4$:xMn$^{4+}$ phosphor was synthesized by high temperature solid-phase method and its luminescence characteristics were explored. The X-diffraction pattern measured by the X-ray diffractometer matched well with the international standard card. The synthesized sample is a pure phase crystal, indicating that the doping of Mn$^{4+}$ has not changed the crystal structure of K$_2$MgSiO$_4$. Through the excitation and emission spectra measured by the fluorescence spectrometer, it can be seen that the sample has 4 excitation peaks at 368nm, 422nm, 451nm and 534nm, and the maximum emission peak of the sample is at 654nm. By changing the doping concentration of Mn$^{4+}$ ions, it is found that as the Mn$^{4+}$ concentration increases, the luminescence intensity of the sample increases, and finally the concentration quenching occurs after the concentration exceeds 1%. The chromaticity coordinates of the emission of the sample were measured to prove its role in the market. The chromaticity coordinates of the sample are located in the red light zone and are close to the standard red light. The fluorescence lifetime of Mn$^{4+}$ transition on the D layer in the sample is about 0.2ms.

1. Introduction

In today's global energy crisis, LED lamps with high luminous efficiency, energy saving, environmental protection, and long life have replaced traditional lighting devices with short life, high energy consumption and environmental pollution (such as incandescent lamps and fluorescent lamps) have become widely used lighting devices [1]. Today's commercial white LED lamps are mostly blue LEDs covered with yellow phosphors to obtain white LED lamps [2, 3]. However, such white light LEDs lack red light components, resulting in low color rendering index and high color temperature. This limits its development in the field of lighting, so we need an excellent red phosphor to supplement its missing red light component [4].

Rare earth ions are widely studied and applied due to their red light emission due to their excellent luminescence properties. Although my country is a large rare earth country, rare earths are a limited resource. It is expensive, and the use of rare earth-doped red phosphors increases the cost of white LEDs. Therefore, it is important to find other cheap non-rare-earth element-doped red phosphors.

As a transition element, Mn has good optical properties. Mn$^{4+}$ has 3d$^5$ electron orbits and has a strong absorption peak in the 300-500nm band. This transition is a spin-allowed transition, which can appear narrow peak red light emission and be emitted by near ultraviolet and blue light. Excitation, it can be effectively excited by near-ultraviolet LED and blue LED and used in white LED [5, 6], and Mn$^{4+}$ do...
ped phosphor has high stability, high chromaticity and high luminous efficiency. Therefore, it is of great significance to study the new type of Mn⁴⁺ doped red phosphor.

2. Experiment methods
Prepare K₂MgSiO₄: xMn⁴⁺ phosphor by high temperature solid phase reaction method. Weigh MgO according to the stoichiometric ratio, mix K₂CO₃ and MgO₂, then put it in an agate mortar and grind it evenly, then put it in a corundum crucible and place it in a tube furnace under air atmosphere. The temperature was raised to 1400°C for 6 hours, and the sample was taken out after being naturally cooled to room temperature to obtain a K₂MgSiO₄:Mn⁴⁺ sample.

The X-ray diffractometer of Japan Rigaku Ultra IV model (tube pressure is 40kV, tube flow is 40mA, λ=1.5418Å excitation source is CuKα target) was used to determine the XRD pattern of the sample. Using Edinburgh FS5 full-function fluorescence spectrometer (UK), 150W xenon lamp was used as the excitation source, and the excitation, emission spectra and fluorescence lifetime curves of the samples were measured at room temperature.

3. Results and Discussion
Figure 1 depicts the XRD pattern of the K₂MgSiO₄:xMn⁴⁺ (x=0.005, 0.01, 0.02, 0.04) series of samples. From Figure 1, it can be seen that the comparison with the international standard card of K₂MgSiO₄ (PDF NO.39-1426) is basically consistent. It shows that we made pure phase K₂MgSiO₄ crystal. And it can be seen from the figure that the experimental doping concentration changes did not cause obvious changes in the crystal structure. In comparison, we find that the diffraction peak shifts to the right. According to the Bragg formula (2d sin θ = nλ): n and h are fixed, so the angle shift is caused by d, indicating that Mn⁴⁺ with a smaller ion radius replaces the larger ion radius in the K₂MgSiO₄ crystal. Mg²⁺ becomes the luminescence center.

Figure 1. XRD pattern of K₂MgSiO₄:xMn⁴⁺ (x=0.005, 0.01, 0.02, 0.04) phosphor.

Figure 2 shows the excitation spectrum of the K₂MgSiO₄:xMn⁴⁺ (x=0.005, 0.01, 0.02, 0.04) series of samples. In the figure, the shape of the excitation peak does not change with the change of Mn⁴⁺ doping concentration, only the excitation intensity occurs. In the figure, we can see that when the doped Mn⁴⁺ ion concentration is 1%, the excitation intensity is the largest. The main excitation of the sample is located in the 368 nm ultraviolet region, 422 nm violet region, 451 nm blue region and 534 nm green region. The 368 nm excitation is due to Mn⁴⁺ replacing Mg²⁺, which leads to the charge imbalance, resulting in the CT transition of Mn⁴⁺—O²⁻. The excitation at 422nm, 451nm and 534nm are
the charge transitions of Mn$^{4+}$ $^4A_2g$-$^4T_{1g}$, $^4A_2g$-$^4T_{2g}$ and $^4A_2g$-$^2T_{2g}$, respectively. The excitation with a wavelength of 451nm matches well with the commercial blue LED dies currently on the market [7].

Figure 2. Excitation of K$_2$MgSiO$_4$:xMn$^{4+}$ (x=0.005, 0.01, 0.02, 0.04) phosphor under 654 nm emission.

As shown in Fig. 3, when the samples of this series are excited by blue light with a wavelength of 451nm, the peak shapes of the emission spectra under different doping concentrations are basically similar, but the emission intensity is quite different. Its strongest peak is about 654nm, which corresponds to the energy level transition from the lowest excited state $^2E_g$ of Mn$^{4+}$ to the ground state $^4A_{2g}$. I can see that the emission intensity is the highest when the doping concentration of Mn$^{4+}$ is 1%, and when the doping concentration exceeds 1%, the emission intensity of the sample is quenched by the concentration effect and the emission intensity begins to decrease.

Figure 3. The emission spectrum of K$_2$MgSiO$_4$:xMn$^{4+}$ (x=0.005, 0.01, 0.02, 0.04) phosphor under the excitation of 451nm.
Figure 4 shows the fluorescence lifetime decay curve of K2MgSiO4:xMn4+ series samples when the monitoring wavelength is 654 nm and the excitation wavelength is 422 nm. In the figure, we can see that there is no obvious change in the fluorescence lifetime decay curve under different concentrations of Mn4+ doping. According to the decay curve formula:

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

(1)

where $\tau$ represents the fluorescence lifetime, $I$ represents the fluorescence intensity at time $t$, and $A$ represents the fluorescence intensity at the initial moment. Fitting the attenuation curve to calculate the fluorescence lifetime of the sample is 0.187 ms, 0.190 ms, 0.214 ms and 0.219 ms, corresponding to the doping concentration 0.5%, 1%, 2% and 4%. All the results are within microseconds, indicating that the transition of Mn4+ in the d layer is a forbidden transition [8, 9], its time in the excited state is short and the luminous efficiency is high.

![Figure 4. K2MgSiO4: xMn4+ (x=0.005, 0.01, 0.02, 0.04) phosphor fluorescence decay curve.](image)

We calculated the color coordinates of the K2MgSiO4: xMn4+ (x=0.005, 0.01, 0.02, 0.04) series of samples under the excitation of 451 nm wavelength with CIE1931 color coordinate software. As shown in Figure 5, the coordinates are basically similar with the change of concentration. (0.68, 0.31). The chromaticity coordinates of the sample are close to the red light standard value (0.67, 0.33) specified by NTCE [10], so it has a great use value in the market.
4. Conclusion
In this paper, a high-temperature solid-phase method is used to prepare K$_2$MgSiO$_4$:xMn$^{4+}$ (x=0.005,0.01,0.02,0.04) series of fluorescent materials. XRD patterns show that doped Mn$^{4+}$ replaces Mg$^{2+}$ as the luminescent center. The excitation of the sample at a wavelength of 451 nm can be used for commercial blue LED excitation. The highest emission peak of the sample is located at the wavelength of 654 nm. The emission intensity of the sample increases with the increase of the Mn$^{4+}$ doping concentration. When the concentration reaches 1%, the emission intensity is the highest. After the concentration is increased, the concentration quenching will cause the emission intensity to decrease. The emission of the sample shows very close to the international red standard value on the chromaticity coordinates. The fluorescence lifetime of the transition of Mn$^{4+}$ on the d layer in the sample is within microseconds, so its time in the excited state is short, and its luminous efficiency is high.

Acknowledgments
This work was supported by the National Natural Science Foundation of China (21661036).

References
[1] Chen Qiaoling, Lü Shaozheng. White light emission in Pr$^{3+}$, Tb$^{3+}$:CaYAlO$_4$ phosphor[J]. Optoelectronics Letters, 2015, 11(05):370-374.
[2] Feng Liu, Zhenwei Pan, Jiahua Zhang, Xiaojun Wang. White LED solid-state lighting based on phosphor light conversion[J]. The Chinese Journal of Rare Earths, 2017, 35(02):171-182.
[3] Lü Wei, Jiao Mengmeng, Shao Baiqi, et al. Enhancing photoluminescence performance of SrSi$_2$O$_2$N$_2$:Eu$^{2+}$ phosphors by Re (Re = La, Gd, Dy, Lu, Sc) substitution and its thermal quenching behavior investigation. Inorganic Chemistry, 2015, 54(18):9060-5.
[4] Zhiping Yang, Wang Tianyang, Ran Zhengrui. Preparation and luminescence properties of K$_2$MgSiO$_4$: Eu$^{3+}$ red phosphor[J]. Optoelectronics-Laser, 2016, 27(07):730-734.
[5] Nguyen H D, Lin C C, Fang M H, et al. Synthesis of Na$_2$SiF$_6$: Mn$^{4+}$ red phosphors for white LED-applications by co-precipitation[J]. J. Mater. Chem. C., 2014, 2:10268-10272.
[6] Wu Yonghua, Yang Fugui, Qiao Liang, Ren Haike. Study on the luminescence characteristics of...
non-rare earth red phosphor Mn~(4+): Li2TiO3[J]. Optoelectronics-Laser, 2017, 28(08): 854-858.

[7] Jiang Xianyu, Chen Zhen, Huang Shaoming, et al. A red phosphor BaTiF (6): Mn(4+): reaction mechanism, microstructures, optical properties, and applications for white LEDs.. Dalton Transactions, 2014, 43(25):9414-8.

[8] Fu A.J., Pang Q, Yang H., et al. Ba2YNbO6:Mn4+-based red phosphor for warm white light-emitting diodes (WLEDs):Photoluminescent and thermal characteristics[J].Optical Materials,2017,70:144-152.

[9] Chen Caihua, Yang Guohui, Liang Lifang, Meng Lili, Zhang Lixia. Sol-gel synthesis of CaYAlO4: Mn~(4+) red phosphor and its fluorescence properties[J]. Acta Luminescence, 2017, 38(05) :567-573.

[10] He Xiaolin, Yang Dingming, Hu Wenyuan, Liao Qilong. Preparation of Li2ZnSiO4: Eu~(3+) red phosphor and its luminescence properties[J]. Journal of the Chinese Ceramic Society, 2014, 42(03): 309-313.