LUMINESCENCE PERFORMANCE OF RED PHOSPHOR $K_2ZnSiO_4: Eu^{3+}$ FOR BLUE CHIP

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A high intense red-emitting phosphor $K_2ZnSiO_4: Eu^{3+}$ peaking at 593-616 nm was synthesized by high-temperature solid-phase method. Multiple techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM) are used to examine the surface morphology and structural properties of $K_2ZnSiO_4: Eu^{3+}$ phosphors. The excitation wavelength matches well with that of the emission of the blue-light emitting diode. The emission peaks at 593 and 616 nm are attributed to $Eu^{3+}$5D$_0$-7F$_1$, 5D$_0$-7F$_2$, respectively.

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1. Introduction

A light revolution is sweeping all over the world since it has advanced properties such as long life time, low energy consumption, high efficiency, environmentally friendliness and their potential applications in indicators, backlights, automobile head-lights and general illuminations[1,2]. In the context of energy and environmental protection, the development of LED are taken into attention. Commercially available white light emitting diodes(WLED) consist of a GaN based on ultraviolet(UV) blue LED along with a coating of yellow phosphor namely, and $Ce^{3+}$ doped Yttrium Aluminum Garnet (YAG:Ce$^{3+}$)[3–7]. However, this white light has a poor heat resistance, high correlated color temperature and low color rendering index due to their low thermal quenching temperature and lack of red emitting element [4–9]. These shortcomings limit its prospects in the field of WLED lighting [10,11]. Thereore, it is critical to add a red-emitting phosphor to compensate the deficiency[12,13].

It is well known that a suitable blue-LED phosphor should have a stable host, exhibit strong absorption around 455 nm and show strong emission under 455 nm excitation. The current red phosphors for WLEDs based on GaN-LEDs is $(Ca_{1-x}Sr_x)S: Eu^{2+}$[14]. However, the red phosphor $(Ca_{1-x}Sr_x)S: Eu^{2+}$ shows lower efficiency and chemical stability under the...

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excitation of blue-light. The thermal chemical stability and coverage a broad emission spectrum of europium-activated nitrogen-containing compound can be excited by blue light and emit red light, but the synthesis process is complex, and high-purity nitride material is more difficult to obtain, so it is difficult to large-scale production[15].

Therefore, great efforts have been made to explore good phosphors for application in WLEDs. We have found that K$_2$ZnSiO$_4$:Eu$^{3+}$ has a strong red emitting under the excitation of blue-light, which suggests its potential applications in many fields.

In this study, the K$_2$ZnSiO$_4$:Eu$^{3+}$ phosphors are synthesized by high-temperature solid-phase method, with Eu$^{3+}$ as activator, and their luminescent properties were investigated. These phosphors were excited by blue chip, and emit red light.

### 2. Materials and methods

#### 2.1. Materials Preparation

K$_2$ZnSiO$_4$:Eu$^{3+}$ was synthesized successfully through the conventional high temperature solid state reaction method. All of the chemical reagents used in this experiment were analytical grade. The reactants used in the preparation were K$_2$CO$_3$, Zn(NO$_3$)$_2$·6H$_2$O, SiO$_2$, Eu$_2$O$_3$. The stoichiometric amount of starting materials was weighed out and then mixed and milled thoroughly for 1 h in an agate mortar. Afterwards, the mixtures were transferred into corundum crucibles and prefired at 500°C for 1 h in a furnace. After cooling down naturally to room temperature, they were ground again for 30 min and finally calcined at 950°C for 4 h in furnace.

#### 2.2. Analysis Methods

The structures of the phosphor were established by X-ray diffractometer (XRD) (Shimadzu, XRD-6000, Cu Kα target) and the morphology of the particles was observed by field emission scanning electron microscope (FE-SEM) (Sirion 200, Philip). The photoluminescence properties of the phosphors were studied on fluorescence spectrophotometer (Shimadzu, model RF-5301 PC). All the photoluminescence properties of the phosphors were measured at room temperature.

### 3. Result and Discussion

#### 3.1. Phase characterization and SEM

To determine the phase purity of the samples, XRD measurements for the synthesized products were conducted. Figure 1 shows the XRD patterns of K$_2$ZnSiO$_4$:Eu$^{3+}$. The XRD patterns of samples were consistent with JCPDS standard card(JCPDS.39-0268). No impure phases such as K$_2$CO$_3$, Zn(NO$_3$)$_2$·6H$_2$O, SiO$_2$ were observed, indicating that the doping Eu$^{3+}$ ions did not influence the crystal structures of phosphors. According to the standard card JCPDS(No.39-0268),we see that K$_2$ZnSiO$_4$ belong to a cubic system, and the lattice parameter is a=7. 688 nm. Figure 2 shows the SEM images of material calcined at 950°C for 4
h, from which we can see the samples are single phase and have irregular shape.

![XRD pattern](image1.png)

*Fig. 1: The XRD patterns of the K$_2$ZnSiO$_4$: Eu$^{3+}$*

![SEM image](image2.png)

*Fig. 2: SEM image of material*

### 3.2. Luminescent properties analysis

The excitation spectra and emission spectra of K$_2$ZnSiO$_4$: Eu$^{3+}$ phosphors are given in Fig. 3. The excitation spectrum was under 616 nm emission and the emission spectra was under 466 nm excitation. The excitation spectrum (curve a) extends at 394 nm and 466 nm, which is due to $^7\!F_0\rightarrow ^5\!L_6$ and $^7\!F_0\rightarrow ^5\!D_2$ transitions of the Eu$^{3+}$, respectively. The transition at 466 nm was the strongest absorption, which is corresponding to the excitation of blue chip. The emission spectrum (curve b) shows that there are two main emission peaks located at 593 nm and 616 nm, corresponding to Eu$^{3+}$ $^5\!D_0\rightarrow ^7\!F_1$, $^5\!D_0\rightarrow ^7\!F_2$, respectively[16]. Both the two emission peaks belong to the f-f characteristics emission transition of Eu$^{3+}$, and the strong emission peak locates at 616 nm, and the samples emit a significant red light. According to
multi-electron atom spectral election, the electric dipole transition between $^5\text{D}_0-^7\text{F}_2$ is forbidden, and that Eu$^{3+}$ occupies asymmetric inversion center in the crystal is favorable to improve the luminance, and the magnetic dipole transition of $^5\text{D}_0-^7\text{F}_1$ is allowed, and Eu$^{3+}$ in the central symmetry sites is beneficial to improve the luminance. By calculating, we see that Eu$^{3+}$ occupies non-centrally symmetric matrix sites. From figure 3, we can see that the intensity of red light located at 616 nm is stronger than the orange light located at 593 nm. This is because the forced electric dipole transitions is sensitive to the change in the crystal field, as Eu$^{3+}$ deviates from the crystal inversion center, parity forbidden, and the transition between $^5\text{D}_0-^7\text{F}_2$ is dominant.

![Intensity vs Wavelength Graph](image)

Fig. 3: The excitation($\lambda_{\text{em}}=616 \text{ nm}$) and emission($\lambda_{\text{ex}}=466 \text{ nm}$) spectra of the K$_2$ZnSiO$_4$: Eu$^{3+}$ sample

### 3.3. The effect of the calcination temperature

Fig. 4 shows the XRD patterns of K$_2$ZnSiO$_4$: Eu$^{3+}$ sample in different calcination temperature. From which we can see that the diffraction peak of the sample at each temperature are correspond to the standard card, only a little different in the intensity of the diffraction peak. When the temperature rises to 950°C, impurity phases disappear, and diffraction peaks become to be sharp with a high degree of crystallization. With the increasing of calcination temperature, the number of diffraction peak is no different, but the shape of diffraction peak become to be dispersed. Under a certain heating condition, increasing the calcination temperature to increase the starting synthesized temperature is positive to the absorbing energy and growth of luminescent material, however, when the calcination temperature is too high, too much energy lead to fast growth of luminescent material, and impurities exit in luminescent material, thus reducing the crystallization.
Figure 5 presents emission spectra of luminescent materials under different calcination temperature. With the increasing of calcination temperature, the shape of the emission spectrum has no significant differences, only the intensity has a trend from increasing to decreasing, and the intensity when the temperature reaches 950°C with the fluorescence intensity is the best, which is consistent with the result of XRD.

3.4. The effect of the calcination time

Fig. 6 shows the XRD patterns of K₂ZnSiO₄:Eu³⁺ sample in different calcination time. When the raw material was under calcinations, the characteristic diffraction peaks are clear and correspond to the standard card. However, with the different calcination time, diffraction curve has a little differences. When the calcination time is too short, the main diffraction peak
of luminescent materials becomes diffuse and lacks of sharpness, with the increasing of calcination time, the crystallization of luminescent materials improved significantly, and 3 h is the best for the parameters of the shape of diffraction peak, sharpness and WFM. With the continued increasing of calcination time, the energy of material absorbing is too much for crystal composition and growth, and the excess energy plays a negative role in increasing the crystal internal stress, then it results in excessive growth of luminescent materials and the internal energy is released, thus it results in crystal lattice distortion.

Fig. 6: The XRD patterns of $\text{K}_2\text{ZnSiO}_4: \text{Eu}^{3+}$ sample at different calcination time

Fig. 7 shows emission spectra of luminescent materials under different calcination time. As can be seen, the basic shape of the emission spectrum and the position of main emission peak have no changes under different calcination time, but emission intensity has a trend to increasing. When the calcining time reaches 3 h, the emission peak reaches to the strongest value. And when the calcining time is more than 3 h, the fluorescence intensity decreases, which is consistent with the result of XRD.

Fig. 7: The emission spectra of luminescent materials under different calcination time
3.5. The effect of the different concentrations of Eu$^{3+}$

Fig 8 shows the emission spectra of K$_2$ZnSiO$_4$:Eu$^{3+}$ phosphors as the different doping of Eu$^{3+}$. We can see that the position and shape of the emission peak have no changes, but the emission intensity has a significant change. When the concentration of Eu$^{3+}$ is in a low level, the luminescent center is less, and the luminescence intensity of sample is weak. With the increasing of Eu$^{3+}$, Eu$^{3+}$ occupies non-inversion center position, and electric dipole transition of $^5D_0$-$^7F_2$ gradually increased, and the emission intensity of the sample increases. What we see an interesting thing is that the concentration range in the experimental determination (from 4% to 14%) did not appear the phenomenon of concentration quenching. The reason may be that K$_2$ZnSiO$_4$ matrix has some unique lattice structure, and dopant ions Eu$^{3+}$ arranged a one-dimensional or two-dimensional in K$_2$ZnSiO$_4$ matrix, thus inhibiting the excitation energy transfer re-migration, so concentration quenching does not occur[17].

![Fig. 8: Emission spectra of different concentrations of Eu$^{3+}$ doping.](image)

4. Conclusions

The Eu$^{3+}$ doped K$_2$ZnSiO$_4$ phosphor was synthesized by high-temperature solid-phase method, and the doped of Eu$^{3+}$ studies to evaluate the effect of luminescence. The K$_2$ZnSiO$_4$ we synthesized belong to cubic crystal system, and the excitation peak located at 394 nm and 466 nm attributed to f-f characteristic transitions of Eu$^{3+}$. The photoluminescence properties of K$_2$ZnSiO$_4$: Eu$^{3+}$ indicate that these phosphors emitted red light under excitation of 466 nm, and among them Eu$^{3+}$ was used as activator, and the emission intensity increased with the adding of Eu$^{3+}$, and there is no concentration quenching phenomenon in the experimentally measured concentration range. When the phosphor combined with a blue LED chip, the sample can be well applied to WLED.
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References