

Luminescent characteristics of $\text{Sr}_2\text{ZnSi}_2\text{O}_7 : \text{Eu}^{3+}$ phosphor for ultraviolet light emitting diodes

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Red-emitting phosphors $\text{Sr}_{2-x}\text{ZnSi}_2\text{O}_7 : \text{Eu}_x^{3+}$ was prepared by a combustion-assisted synthesis method and an efficient red emission under near-ultraviolet (UV) was observed. The luminescence, crystallinity, and particle sizes were investigated using luminescence spectrometry, X-ray diffractometry, and field scanning electron microscopy. The emission spectrum shows that the most intense peak is located at 614 nm, which corresponds to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} . The phosphor has two main excitation peaks located at 394 and 465 nm, which match the emission of UV and blue light-emitting diodes, respectively.

Key words: Optical properties, Chemical synthesis, Luminescence.

Introduction

Remarkable progresses have been observed in the development of white light emitting diodes (WLEDs) using GaN as well as InGaN chips [1-3]. Nowadays, a WLED device has been commendably realized by using $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Ce}$ as a broad band yellow phosphor coated on a blue LED chip [4]. However, there exists at least two drawbacks in this combination. Firstly, the overall efficiency decreases rapidly when the correlated color temperature of the device is lowered. Secondly, a concern with this device is that the “white” output light has an undesirable color balance for a true color rendition. So a separate red light source may be used to compensate for the red deficiency of the output light [5-7]. Another promising possibility is the fabrication of WLEDs by employing red, green and blue emitting phosphors that are excited by an ultraviolet (UV) LED chip [8]. Recently, red phosphors which are activated by Eu^{3+} were extensively reported [9-12], these phosphors can be effectively excited by the 395 nm UV-LED.

The red light emitting phosphor for a UV-LED is, commercially, still limited to the divalent Eu ion activated sulfide [13]. Therefore, a new and stable red phosphor, which can be used for a UV-LED is expected. In recent times, Eu^{3+} -doped hardystonites and akermanites phosphors have been extensively investigated as red phosphors because of their chemical stability. The intensities of Eu^{3+} at around 394 and 465 nm are enhanced obviously in these materials compared with other Eu^{3+} -doped phosphors [14-19].

The synthesis method of the commercial phosphor is a

conventional high-temperature solid-state reaction, which is known to be very slow [20], and recently by a hydrothermal synthesis method [15]. Here we report on the synthesis and characterization of red emitting $\text{Sr}_2\text{ZnSi}_2\text{O}_7 : \text{Eu}^{3+}$ powders by a combustion-assisted synthesis method and investigate their luminescent properties.

Experimental

Powder samples with the general formula $\text{Sr}_{2-x}\text{ZnSi}_2\text{O}_7 : \text{Eu}_x^{3+}$ ($x = 0-0.09$) phosphor were prepared by the combustion synthesis method. $\text{Si}(\text{OC}_2\text{H}_5)_4$ (analytical grade) was used as a silica source for the combustion synthesis. The starting materials were $\text{Sr}(\text{NO}_3)_2$ (analytical grade), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (analytical grade), $\text{Si}(\text{OC}_2\text{H}_5)_4$ (analytical grade), Eu_2O_3 (99.99%), NH_2CONH_2 (analytical grade) and H_3BO_3 (analytical grade). NH_2CONH_2 was added as a fuel and H_3BO_3 was a flux, respectively. Eu_2O_3 was dissolved in HNO_3 to convert into a $\text{Eu}(\text{NO}_3)_3$ solution completely. The appropriate molar ratio of $\text{Sr}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3$, NH_2CONH_2 and H_3BO_3 were dissolved in a minimum amount of distilled water to produce a clear solution. Then a stoichiometric amount of $\text{Si}(\text{OC}_2\text{H}_5)_4$ dissolved in ethanol was added dropwise into the above solution under vigorous stirring. $\text{Si}(\text{OH})_4$ was formed by the hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ as follows:



The mixed solution was allowed to react at 80 °C for 2 h to obtain a homogenous solution. And then the solution was introduced into a muffle furnace preheated at 600 °C. Within a few minutes, the solution boiled and was ignited to produce a self-propagating flame. The product obtained was post-annealed at various temperatures ranging from 800 to 1100 °C for 3 h.

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The synthesized phosphors were ground to powder and passed through a 200 mesh sieve prior to the characterization. The crystal phase of the synthesized powders prepared in the process was characterized by X-ray powder diffraction using an X Pert PRO X-ray diffractometer having a Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV tube voltage and 40 mA tube current. The XRD patterns were collected in the range of $10^\circ \leq 2\theta \leq 90^\circ$. The morphology was observed using a Quanta 400 (FEI, Holland) field-emission scanning electron microscopy (FE-SEM). The emission spectrum was taken on an RF-5301 (Shimadzu, Japan) fluorescence spectrophotometer equipped with a xenon discharge lamp as an excitation source. The excitation and emission slits were set to 3.0 nm. All the above measurements were taken at room temperature.

Results and Discussion

Fig. 1 shows the phase identifications of the $\text{Sr}_{1.95}\text{ZnSi}_2\text{O}_7 : \text{Eu}_{0.05}^{3+}$ powders heat-treated for 3 h as a function of heating temperature using XRD. The diffraction peak positions and the relative intensities of the samples prepared are well matched with that in the literature [21]. There are no observable differences between the two diffraction patterns, indicating that the small amount of doped rare-earth ions has almost no effect on the $\text{Sr}_2\text{ZnSi}_2\text{O}_7$ crystalline structure. Its diffraction peak is consistent with the standard JCPDS card of tetragonal $\text{Sr}_2\text{ZnSi}_2\text{O}_7$ phase (JCPDS, 39-0235) and also with that reported in the literature (space group $P421_m$, $a = 8.007 \text{ \AA}$, $c = 5.168 \text{ \AA}$). As evident from the XRD data, a mixture of Sr_2SiO_4 and $\text{Sr}_2\text{ZnSi}_2\text{O}_7$ is obtained when the post-annealing temperature is low 900°C . The Sr_2SiO_4 phase progressively disappeared and a single-phase $\text{Sr}_2\text{ZnSi}_2\text{O}_7$ was achieved with an increase of the post-annealing temperature.

The $\text{Sr}_2\text{ZnSi}_2\text{O}_7$ crystal structure consists of $[\text{ZnO}_4]$ tetrahedral that share their oxygen atoms with those of the $[\text{Si}_2\text{O}_7]$ groups. Calculations of the radius percentage difference (Dr) between the doped ions (Eu^{3+}) and the possible substi-

tuted ions (Sr^{2+} , Zn^{2+}) in $\text{Sr}_2\text{ZnSi}_2\text{O}_7$ are summarized in Table 1. The values are based on the following formula: $Dr = [Rm(CN) - Rd(CN)]/Rm(CN)$, where CN is the coordination number, $Rm(CN)$ is the radius of the host cation, and $Rd(CN)$ is the radius of the doped ion. We take the data of Eu^{3+} with CN = 6 as a reasonable approximation [22]. The value of Dr between Eu^{3+} and Sr^{2+} is 15.40%, while that between Eu^{3+} and Zn^{2+} is -57.83%. Thus, doping ions of Eu^{3+} will preferentially substitute the strontium sites.

Fig. 2 shows the emission spectra of $\text{Sr}_{1.95}\text{ZnSi}_2\text{O}_7 : \text{Eu}_{0.05}^{3+}$ powders prepared at different post-annealing temperatures in the range of $800\text{--}1100^\circ\text{C}$. The phosphor particles prepared at 800°C had a lower photoluminescence intensity because of their poor crystallinity. The emission intensity increases with an increase of the post-annealing temperature, because of the improvement in crystallinity. However, the emission intensity decreases when the post-annealing temperature further increases to 1100°C . This may be due to excessive sintering and aggregation of particles, which agrees with the result obtained from SEM observations.

Fig. 3 displays a typical FE-SEM result of the phosphors synthesized at 1000°C (Fig. 3a) and 1100°C (Fig. 3b). The micrographs reflect the basic particle morphology, where the smallest particle could be identified with a crystal and/or their aggregates. The particle sizes increase with an increase in the temperature because a higher temperature can significantly promote the growth of $\text{Sr}_{1.95}\text{ZnSi}_2\text{O}_7$:

Table 1. Ionic radii difference percentage (Dr) between matrix cations and doped ions

Doped ions	Rd(CN) (Å)	Dr = [Rm(CN)-Rd(CN)]/Rm(CN) (%)	
		$R_{\text{Sr}^{2+}}(8) = 1.26 \text{ (Å)}$	$R_{\text{Zn}^{2+}}(4) = 0.60 \text{ (Å)}$
Eu^{3+}	0.947(6)		-57.83
	1.066(8)	15.40	

CN stands for coordination number, Rm(CN) and Rd(CN) for the radii of matrix and doped cations, respectively, and the data of the effective ionic radii are from Ref. [23]

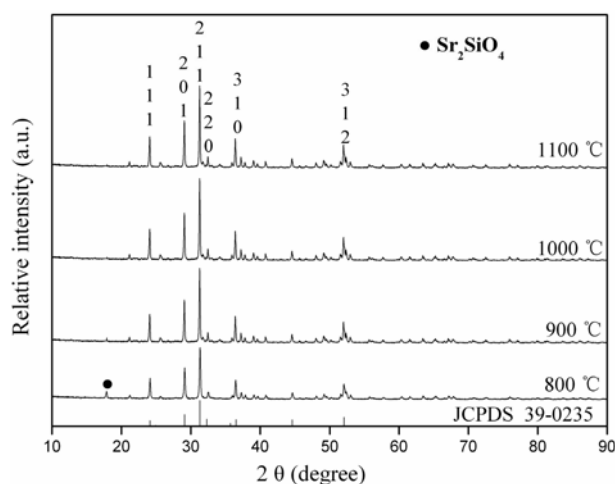


Fig. 1. X-ray diffraction patterns of $\text{Sr}_{1.95}\text{ZnSi}_2\text{O}_7 : \text{Eu}_{0.05}^{3+}$ phosphors.

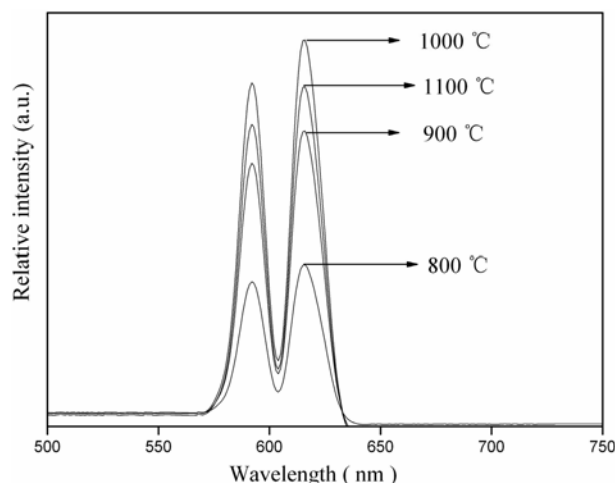


Fig. 2. Emission spectra of $\text{Sr}_{1.95}\text{ZnSi}_2\text{O}_7 : \text{Eu}_{0.05}^{3+}$ at different temperatures ($\lambda_{\text{ex}} = 394 \text{ nm}$).

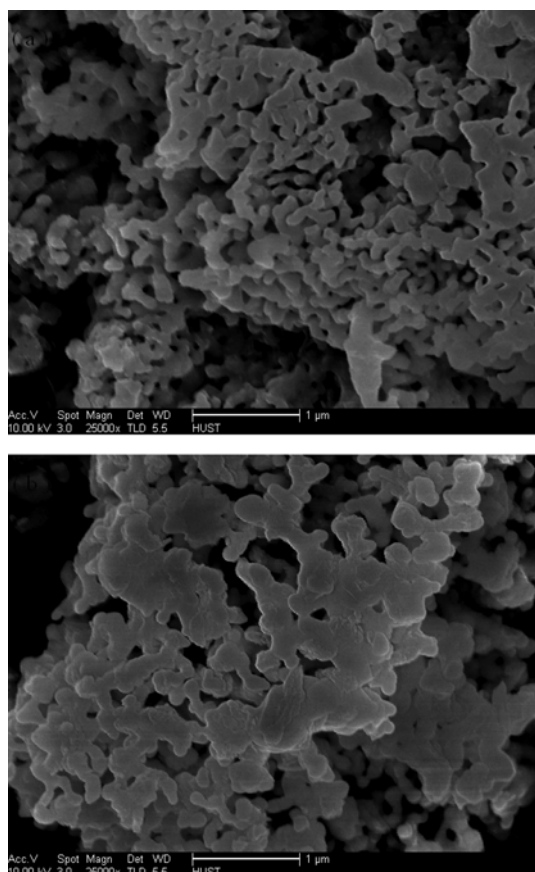


Fig. 3. SEM photograph of particles prepared at 1000 °C (a), 1100 °C (b).

$\text{Eu}_{0.05}^{3+}$ particles and lead to excessive sintering and aggregation of particles.

The effect of Eu^{3+} concentration on excitation and emission spectra of $\text{Sr}_2\text{ZnSi}_2\text{O}_7 : \text{Eu}^{3+}$ phosphors is shown in Fig. 4, in which the Eu^{3+} concentration varies from 0.01 mol to 0.09 mol. It can be observed that the emission intensities increase because of the concentration quenching, and the maximum value is at 0.05 mol Eu^{3+} .

Dexter proposed that the interaction type between sensitizers or between sensitizer and activator can be determined by $\lg(I/x) = c - (\theta/3)\lg x$ when the concentration is high enough [24]. Among the concentration quenching mechanisms caused by the electric multipole interaction, the dipole-dipole (d-d), dipole-quadrupole (d-q) and quadrupole-quadrupole (q-q) interactions correspond to $\theta = 6, 8, 10$, respectively. I is the luminescence intensity of the $\text{Sr}_2\text{ZnSi}_2\text{O}_7 : \text{Eu}^{3+}$ phosphor, and x is the Eu^{3+} concentration. According to this proposal, the emission intensities of $\text{Sr}_2\text{ZnSi}_2\text{O}_7 : \text{Eu}^{3+}$ phosphors were measured with Eu^{3+} concentrations of 1, 3, 5, 7 and 9 mol% and the concentration dependence curves ($\lg(I/x) - \lg x$) are shown Fig. 5. According to the linear slope, $\theta = 6.45 \approx 6$. This result indicates that the concentration self-quenching mechanism of Eu^{3+} in $\text{Sr}_2\text{ZnSi}_2\text{O}_7$ is the d-d interaction.

Fig. 6 shows the emission spectra under 394 or 465 nm excitation, which means that this phosphor can be effectively

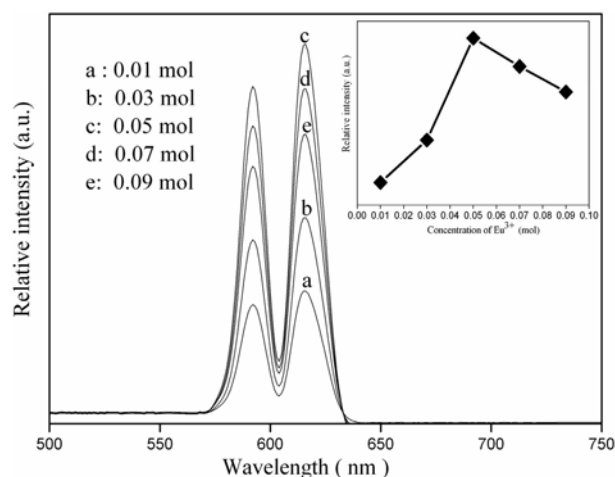


Fig. 4. Emission ($\lambda_{\text{ex}} = 394$ nm) intensity of $\text{Sr}_{2-x}\text{ZnSi}_2\text{O}_7 : \text{Eu}_x^{3+}$ with different Eu^{3+} concentrations.

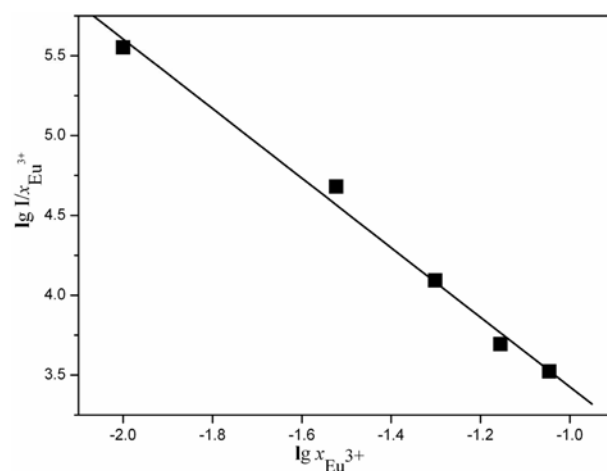


Fig. 5. Plot of $\lg(I/x_{\text{Eu}^{3+}})$ as a function of $\lg x_{\text{Eu}^{3+}}$ in $\text{Sr}_{2-x}\text{ZnSi}_2\text{O}_7 : \text{Eu}_x^{3+}$ phosphors ($\lambda_{\text{ex}} = 394$ nm).

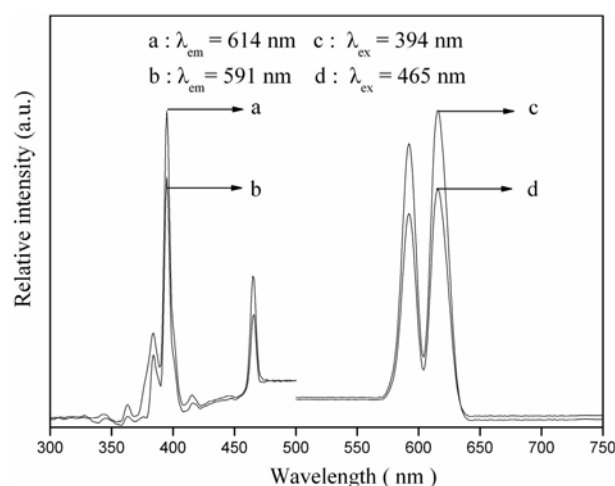


Fig. 6. Photoluminescence spectra of $\text{Sr}_{1.95}\text{ZnSi}_2\text{O}_7 : \text{Eu}_{0.05}^{3+}$.

excited by UV or blue LED chips. The $\text{Sr}_2\text{ZnSi}_2\text{O}_7 : \text{Eu}^{3+}$ phosphor is a separate red light for the white LED that can be fabricated by employing red, green and blue emitting

phosphors excited by a UV chip, and can compensate for the red deficiency of the output light of the white LED that was combined with a blue InGaN chip. So the $\text{Sr}_{1.95}\text{ZnSi}_2\text{O}_7 : \text{Eu}^{3+}$ phosphor is a promising red phosphor for white LEDs.

Conclusions

$\text{Sr}_{1.95}\text{ZnSi}_2\text{O}_7 : \text{Eu}_{0.05}^{3+}$ red phosphors could be synthesized by a combustion-assisted synthesis method. The photoluminescence spectrum of $\text{Sr}_{1.95}\text{ZnSi}_2\text{O}_7 : \text{Eu}_{0.05}^{3+}$ contains broad excitation bands extending from 300 to 500 nm, resulting from the strong crystal field imposed on the Eu sites. The intensity of emission enhances while the concentration of Eu^{3+} increases. Under ultraviolet and visible excitation, $\text{Sr}_{1.95}\text{ZnSi}_2\text{O}_7 : \text{Eu}_{0.05}^{3+}$ shows a red emission band at 614 nm. We have demonstrated that the optimized phosphor $\text{Sr}_{1.95}\text{ZnSi}_2\text{O}_7 : \text{Eu}_{0.05}^{3+}$ is potentially useful as red phosphor for light-emitting diodes according to its excellence in the excitation spectrum profile.

Acknowledgement

This work was supported by the Natural Science Foundation of China (No.50574042), the Natural Science Foundation of Hubei Province of China (No.2008CB252), and by the Scientific Research Foundation for the Returned Overseas Chinese Scholar, State Education Ministry.

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