Effect of C$_3$N$_6$H$_6$ on Luminescent Properties of SrSi$_2$N$_2$O$_2$:Eu$^{2+}$ Yellow Phosphors Prepared by Microwave Reaction Method

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Abstract

In this paper, SrSi$_2$N$_2$O$_2$:Eu$^{2+}$ yellow phosphors were prepared by microwave reaction method with C$_3$H$_6$N$_6$ as a nitrogen source. The structural properties were studied by X-ray diffraction. The results show that: Eu$^{2+}$ ions in SrSi$_2$N$_2$O$_2$ system form a continuous solid solution. The broad intense excitation is from 5d-4f transition of Eu$^{2+}$ ions, ranging from 350 to 470nm. Yellow light-emitting phosphors with excellent luminescence properties can be obtained by the right proportion of ingredients and sintering for 35min under reduction atmosphere. What's more, C$_3$H$_6$N$_6$ is a must. Increasing the concentration of Eu$^{2+}$ within certain limits can also enhance the luminescent properties. If the flux is felicitous, emission peak will gradually red shift, from yellow green (538nm) to yellow (560nm).

Keywords: LED; Microwave; SrSi$_2$N$_2$O$_2$; Excitation spectra; Nitride

1. Introduction

In recent years, global energy shortage and environmental pollution problems have become increasingly prominent. People are eager to apply the new energy saving technology, while semiconductor lighting (Light Emitting Diode-LED) technology has attracted great interest. They show many advantages over the existing incandescent and halogen lamps in terms of power efficiency, reliability, and long lifetime. Moreover, they present promising features such as compactness, environment friendliness, and...
low maintenance. With the start-up of the National Semiconductor Lighting Project, LED lighting technology will further change our world.

According to recent statistics: the annual electricity consumption of China for lighting is about 250 billion kWh, if replace the traditional lighting by LED lamps, it will save 220 billion kWh each year, which is equivalent to saving three generating capacity of Three Gorges Project [1]. At present, the common way to generate white light is through a combination of blue LED with yellow-emitting phosphors. And it is very important to design new light-conversion yellow phosphors. As a novel class of yellow phosphors, oxynitride materials have received considerable attention because of their potential applications in solid-state lightings and displays [2, 3]. In this paper, we focus on the effect of C3N6H6 on luminescent properties of SrSi2N2O2:Eu2+ yellow phosphors prepared by microwave reaction method.

2. Experimental

The phosphor was synthesized by microwave reaction method. The raw materials were stoichiometric SrCO3 (A.R.), C3H6N6 (A.R.), nano-SiO2 (A.R), Eu2O3(99.99%). The mixed raw materials were preheated at high fire for 15~40min under a carbon monoxide reductive atmosphere, then cooled down to room temperature and grinded the sample. The obtained products were SrSi2N2O2: Eu2+ yellow phosphors. The synthesis conditions were investigated by X-ray powder diffraction (XRD) of Beijing Purkinje General Instrument Corporation. Photo-luminescent excitation and emission spectra were recorded by Fluorescence Spectrometer of Japanese Shimadzu Corporation, model RF-5301PC. All tests were performed at room temperature.

3. Results and discussion

The XRD patterns of SrSi2N2O2: Eu2+ yellow phosphors made by microwave reaction method are shown in Fig. 1. The peaks of phases are very similar with the standard JCPDS card No.49-0840 for SrSi2N2O2 as reference [4, 5]. What’s more, the sample coexists a-Sr2SiO4 (JCPDS 39-1256) phase. Therefore, the result shows a mixture of SrSi2N2O2 and a-Sr2SiO4 phases, and the SrSi2N2O2 phase is dominant.

Fig. 2 presents the excitation (1) and emission spectra (2) of SrSi2N2O2:Eu2+. The emission spectrum of the sample centers around 560nm under a broad band excitation from 350 to 470nm, with the peaks located at 375 and 450nm respectively. The broad excitation spectrum extending from 350 to 470nm is due to the 4f-5d electronic transition of Eu2+. Consequently, this yellow phosphor can be excited efficiently by a UV-, NUV-, or blue-LED chip, which indicates their potential applications in white LEDs.

![Fig. 1. XRD patterns of SrSi2N2O2: Eu2+ yellow phosphors.](image-url)
Since microwave heating is a rapid reaction, the synthesis must be carried out by lively nitride reagents. C$_3$H$_6$N$_6$ is a new, effective and cheap nitride reagent of synthesizing oxynitride phosphors. Therefore, it’s necessary to explore the luminescent properties of the samples sintered by different proportions between C$_3$H$_6$N$_6$ and SiO$_2$. Fig. 3 shows luminescence properties of SrSi$_2$N$_2$O$_2$: Eu$^{2+}$, which sintering by different materials proportions n (C$_3$H$_6$N$_6$): n (SiO$_2$). Through repeated experiments, the emission spectrums display the maximum luminous intensity when the proportions of n (C$_3$H$_6$N$_6$): n (SiO$_2$) is 0.75:1. Within a certain range, the proportions between C$_3$H$_6$N$_6$ and SiO$_2$ of raw materials do not affect the emission center.

Fig. 3. Emission spectra of SrSi$_2$N$_2$O$_2$:Eu$^{2+}$ with different proportions of C$_3$H$_6$N$_6$ and SiO$_2$.

Fig. 4 presents the emission spectra of SrSi$_2$N$_2$O$_2$: Eu$^{2+}$ fired at high temperature for different sintering time, which can be observed a bright yellow color when they were excited by blue light (450nm).

Fig. 4. Emission spectra of SrSi$_2$N$_2$O$_2$:Eu$^{2+}$ for different sintering time.
With the extension of sintering time, light intensity increases, especially from 20min to 25min, light intensity increases significantly. The results show that the samples fired for 35min produce greater emission. Therefore, the sintering time of samples has great influence on luminous intensity.

Fig. 5 shows the emission spectra of SrSi$_2$N$_2$O$_2$: Eu$^{2+}$ phosphors in the range of Eu$^{2+}$ concentrations from 0.4% to 5.4%mol. As can be seen in Fig. 5, the peak emission wavelength is about 555nm upon blue light (450nm) excitation. The emission of Eu$^{2+}$ arises from the transition 5d-4f. The emission intensity of the samples is stronger with the increase of the Eu content. When Eu$^{2+}$ doped concentration at 3.8% mol, the emission intensity becomes maximum value. However, the emission intensity of other samples decreases with the Eu$^{2+}$ concentration on the increase, which can principally be ascribed to concentration quenching. When the Eu$^{2+}$ concentration exceeds the optimum value, Eu$^{2+}$ ions generate strong dipole-dipole interaction with the resonance energy among them arise. What’s worse, most of the radiation channels are close, resulting in emission intensity decrease. Therefore, it is essential to control the Eu$^{2+}$ doped concentration during the preparation of efficient phosphors.

![Fig. 5. Emission spectra of SrSi$_2$N$_2$O$_2$:Eu$^{2+}$ for different Eu concentration.](image)

As we all know, solid-state reaction must be carried out at high temperatures, which is high energy consumption. In addition, less approaches have been used to synthesize oxynitride phosphors, perhaps due to their critical preparation conditions (high temperature, high N$_2$ pressure, and air sensitive starting powders) [6]. However, adding fluxes is an effective means that not only reduce the sintering temperature, but also retain the original properties of the phosphor. Fig. 6 shows the emission spectra of SrSi$_2$N$_2$O$_2$: Eu$^{2+}$ powders with different kinds of fluxes and without flux.

![Fig. 6. Emission spectra of SrSi$_2$N$_2$O$_2$:Eu$^{2+}$ with different kinds of fluxes and $\lambda_{ex} = 450$nm.](image)
As shown in Fig. 6, adding fluxes can effectively reduce the reaction temperature. The emission spectra of phosphors synthesized with different fluxes are similar in shape but different in intensity and emission centers. All the fluxes mentioned in the figure can enhance the emission intensity of SrSi$_2$N$_2$O$_2$:Eu$^{2+}$. KCl and CaCl$_2$ can greatly enhance the luminous efficiency, and the enhancement effect of NH$_4$Cl and BaCl$_2$ is far superior to other fluxes. However, the emission spectra with most of the fluxes are blue shifted, except BaCl$_2$ and CaCl$_2$. In order to improve the Color rendering index, BaCl$_2$ and CaCl$_2$ are of priority. In addition, the emission color of SrSi$_2$N$_2$O$_2$:Eu$^{2+}$ phosphors depends greatly on the fluxes, making it possible to adjust/tune the emission wavelength from a yellow green (538nm) to yellow (560nm) over a wide range by adding different flux. Fig.7 presents the emission spectra of SrSi$_2$N$_2$O$_2$:Eu$^{2+}$ for different fluxes concentrations (a: BaCl$_2$, b: CaCl$_2$). The results show that the samples fired with wt2.5% fluxes produced greater emission. Therefore, to improve the industrial production of white LEDs for general illumination, adding appropriate fluxes must be considered as an important method.

4. Summary

In this paper, SrSi$_2$N$_2$O$_2$:Eu$^{2+}$ yellow phosphors were prepared by microwave reaction method in a hot carbon atmosphere. Discuss the position of excitation spectrum and emission spectrum. Process parameters in preparing SrSi$_2$N$_2$O$_2$:Eu$^{2+}$ yellow phosphors were optimized, such as sintering time, proportion of ingredients. Effects of the addition of flux on spectra were also examined. The emission color of the phosphor can be adjusted/tuned the emission wavelength over a certain range by varying the flux design. It was demonstrated that the emission spectrum of the samples located around 560nm under a broad band excitation from 350 to 470nm, with the peaks located at 375 and 450nm respectively. This yellow phosphor has demonstrated its superior suitability for use in white LEDs and can be excited efficiently by a UV-, NUV-, or blue-LED chip with excellent properties of high luminous efficacy.

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References


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