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Synthesis of High-Brightness Blue-Emitting Phosphors $Sr_2MgSi_2O_7:Eu^{2+}$, Er^{3+} by Gel-Combustion Method Assisted by Microwave and their Properties

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High-brightness blue emitting phosphors $Sr_2MgSi_2O_7:Eu^{2+}$, Er^{3+} were synthesized successfully by gel-combustion method assisted by microwave. The as-synthesized phosphors were analyzed and characterized by X-ray diffraction and fluorescence spectrophotometer. The influences of co-doped Er^{3+} concentration, fuel urea and flux H_3BO_3 on luminescent properties of samples were investigated. The results show that $Sr_2MgSi_2O_7$: Eu^{2+}, Er^{3+} phosphors possess the tetragonal crystal structure similar to that of $Sr_2MgSi_2O_7$. The excitation spectrum shows a broad band from 250 to 450 nm and the strongest excitation peak is at 358 nm. The emission spectrum excited by 358 nm also shows a wide band with the main peak at *ca.* 467 nm, which is ascribed to the typical transition from $4f^65d^1$ to $4f^7$ of Eu^{2+}. It is found that co-doped Er^{3+} can sensitize effectively the luminescence of Eu^{2+} ions in $Sr_2MgSi_2O_7$ host. The luminescence intensity reaches the strongest when the concentration of co-doped Er^{3+} is 0.01, the mass ratio of urea to nitrate is 1.5:1 and the mole fraction of H_3BO_3 is 15 % and it is about 1.3 times of single-doped Eu^{2+} sample.

Key Words: $Sr_2MgSi_2O_7:Eu^{2+}$, Gel-combustion method assisted by microwave, Blue-emitting phosphors, Sensitization effect, Er^{3+}.

INTRODUCTION

In recent years, white light emitting diodes (LEDs) are considered as the new generation of illuminating source and are expected to replace the traditional incandescent, fluorescent and high intensity discharge lamps because of their many advantages of relatively small size, low operating voltage, low energy consumption, long lifetime, high luminous efficiency, relatively low cost of manufacture and environmental-friendly characteristics[1,2].

White light can be generated through the combination of one or more down-converting phosphors and a chip. At present, the most common method to obtain the white light is combining a yellow-emitting phosphor (YAG: Ce^{3+}) with a GaN blue-emitting LED chip[3]. However, this kind of white LEDs shows relatively low colour-rendering index, low luminous efficiency and high colour temperature due to lack of a red-light emitting component[4]. To solve these problems, blue-, green- and red-tricolour phosphors are used and combined with a near ultraviolet (NUV) InGaN chip (350-410 nm) to generate white light. Because the human eyes are not sensitive to NUV light in the range of 350-410 nm, the white colour of this combination only depends on phosphors and the mixture ratio can be varied to adjust the chromaticity of the illuminating source according to different needs. Therefore, these phosphors excited effectively by NUV-LED chips attract extensive attentions[5,6].

Alkaline earth silicate is an excellent matrix for phosphors because of its low cost, stable crystal structure, excellent chemical and thermal stabilization, strong water-persistence compared to other matrixes, so it has been extensively applied in phosphors for LEDs[7-10].

In this paper, $Sr_2MgSi_2O_7:Eu^{2+}$, Er^{3+} phosphors were synthesized by gel-combustion method assisted by microwave. Gelling and drying time were shortened greatly by microwave radiation. The phase structure and luminescent properties of the as-synthesized phosphors were analyzed and characterized by X-ray diffraction and fluorescence spectrophotometer. Moreover, the influences of doping concentration of rare earth ions Er^{3+} and amount of fuel urea and flux H_3BO_3 on the luminescent properties of samples were investigated.

EXPERIMENTAL

The phosphors $Sr_2MgSi_2O_7:Eu^{2+}$, Er^{3+} were synthesized by gel-combustion method assisted by microwave. $Sr(NO_3)_2$ (A.R.), $Mg(NO_3)_2{\cdot}6H_2O$ (A.R.), $Si(OC_2H_5)_4$ (A.R.), anhydrous ethanol (A.R.), Eu_2O_3 (99.9 %) and Er_2O_3 (99.9 %) were employed as raw materials. Small quantities of H_3BO_3 (A.R.) were added as flux. Urea (A.R.) was used as fuel.

The procedure used to prepare $Sr_2MgSi_2O_7:Eu^{2+}$, Er^{3+} is as follows. Firstly, Eu_2O_3 and Er_2O_3 were dissolved, respectively in appropriate nitric acid to form $Eu(NO_3)_3$ and $Er(NO_3)_3$

solution, then their accurate concentration were determined by EDTA complexing titration to ensure a desired stoichiometry. The concentration of $Eu(NO_3)_3$ and $Er(NO_3)_3$ solutions is 0.03838 and 0.0923 mol L^{-1}, respectively. A certain volume of solvent anhydrous ethanol was added into a 100 mL ceramic crucible. According to the nominal composition of target product $Sr_{1.98-x}MgSi_2O_7:Eu^{2+}_{0.02}$, Er^{3+}_x (x = 0, 0.01, 0.02, 0.03, 0.04), stoichiometric $Si(OC_2H_5)_4$, $Sr(NO_3)_2$, $Mg(NO_3)_2{\cdot}6H_2O$, $Eu(NO_3)_3$ and $Er(NO_3)_3$ solution and appropriate amounts of H_3BO_3, urea and distilled water were added in order. Then, the mixture was stirred to make the raw materials dissolve completely. Subsequently, a small amount of HNO_3 (2 mol L^{-1}) was added to adjust pH value of the solution to 2-3. Next, the mixture was treated by ultrasonic wave for 4-5 min to make raw materials mix uniformly. Then, the mixture was put into a WG700SL2011-KG microwave oven and heated under the power of middle-high fire for 4-5 min to evaporate superfluous water fast, initiate hydrolysis and polymerization of $Si(OC_2H_5)_4$ and form a transparent gel. Then the gel was ignited on an electric stove in air atmosphere. This combustion process only took about 1-2 min. After cooling, the dry white loose and porous sample (which was called the precursor) was obtained. Finally, the precursor was ground into fine particles and calcined in muffle furnace under an active carbon atmosphere at 1000 ºC for 75 min to obtain the target product.

Characterization: Phase and crystallization structure of the samples were analyzed and characterized by Y2000 X-ray diffractometer using CuK_α radiation (30 kV × 20 mA and a scanning speed 0.06 º/s). The excitation and emission spectra of the samples were recorded as pellets on a F-380 fluorescence spectrometer. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

XRD Analysis: Fig. 1 shows the XRD pattern of the as-synthesized sample by gel-combustion method assisted by Microwave. Fig. 1 showed that all of the peaks can be indexed to the $Sr_2MgSi_2O_7$ nearly, which agrees well with the JCPDS card (No. 75-1736). According to that, the sample is pure tetragonal phase $Sr_2MgSi_2O_7$ with space group P-421m.

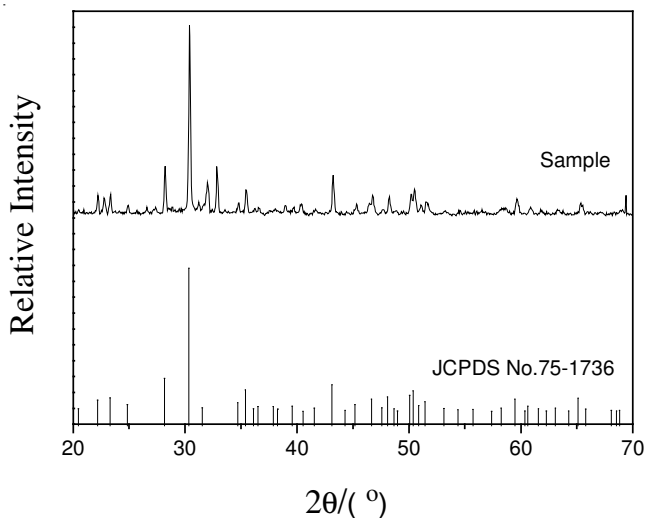

Fig. 1. XRD pattern of as-synthesized $Sr_{1.97}MgSi_2O_7:Eu^{2+}_{0.02}$, $Er^{3+}_{0.01}$

In this pattern, the peaks of compounds of Eu or Er cannot be found, which indicates that Eu^{2+} and Er^{3+} ions have entered into the host lattice and have little effect on the crystal structure of the host $Sr_2MgSi_2O_7$.

The silicate phosphors were usually prepared through traditional solid state reaction method. Lin *et al.*[11] synthesized $M_2MgSi_2O_7$-based (M: Ca, Sr, Ba) long afterglow phosphors by high temperature solid-state reaction under 5 % H_2-95 % N_2 weak reductive atmosphere at 1300 ºC for 3 h. Wu *et al.*[12], synthesized Eu^{3+}-doped $Sr_2MgSi_2O_7$ red-emitting phosphors by high temperature solid-state reaction at 1250 ºC for 2 h. Compared to this method, gel-combustion method assisted by microwave can decrease the calcination temperature and shorten calcination time effectively because of uniform composition and high activity of the precursor.

Excitation and emission spectrum of $Sr_{1.97}MgSi_2O_7:Eu^{2+}_{0.02}$, $Er^{3+}_{0.01}$: The as-synthesized $Sr_{1.97}MgSi_2O_7:Eu^{2+}_{0.02}$, $Er^{3+}_{0.01}$ phosphors can emit high-brightness blue fluorescence by excitation through the ultraviolet ray. The excitation and emission spectrum of $Sr_{1.97}MgSi_2O_7:Eu^{2+}_{0.02}$, $Er^{3+}_{0.01}$ phosphors are shown in Fig. 2. It can be seen that the excitation spectrum of $Sr_{1.97}MgSi_2O_7:Eu^{2+}_{0.02}$, $Er^{3+}_{0.01}$ is a broad band extending from 250 to 450 nm and the main excitation peak is at around 358 nm. Therefore, the phosphors can be excited effectively by NUV-LED chips.

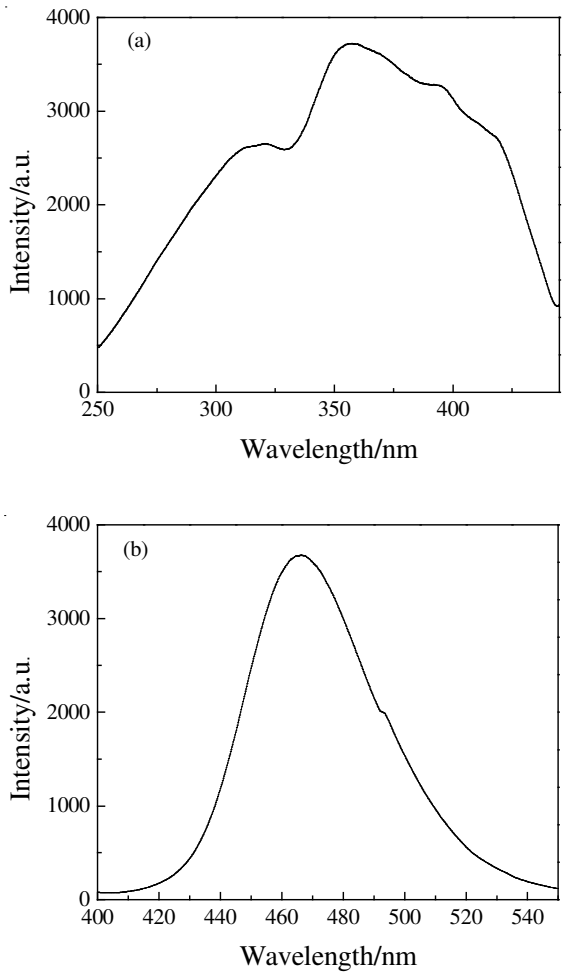

Fig. 2. Excitation spectrum (a) and emission spectrum (b) of $Sr_{1.97}MgSi_2O_7:Eu^{2+}_{0.02}$, $Er^{3+}_{0.01}$

The emission spectrum also shows a broad band with a peak around 467 nm, resulting in blue-emitting, which is assigned to the typical transition[13] $4f^65d^1(t_{2g})$-$4f^7(^8S_{7/2})$ of Eu^{2+}. Because 5*d* electron is an external naked state without being shielded from the 5*s* and 5*p* electrons and the division of its energy level is subject to strong influence of crystal field,the $4f^65d^1(t_{2g}) \rightarrow 4f^7(^8S_{7/2})$ transition of Eu^{2+} exhibits an emission peak with an obvious broad band.

There is no special emission of Er^{3+} and Eu^{3+} in the spectra, which implies that Eu^{3+} ions have been reduced to Eu^{2+} completely and the co-doped Er^{3+} did not emit but transfer the absorbed energy to Eu^{2+} ions in the $Sr_2MgSi_2O_7$ matrix.

Effect of co-doped Er^{3+} concentration on the luminescent properties of $Sr_{1.98}MgSi_2O_7:Eu^{2+}_{0.02}$: In order to investigate the effect of Er^{3+} concentration (x) on luminescent properties of the samples, a series of samples $Sr_{1.98-x}MgSi_2O_7:Eu^{2+}_{0.02}, Er^{3+}_x$ (x = 0-0.04) were synthesized and their excitation and emission spectra are shown in Fig. 3. It can be seen that the Er^{3+} concentration has little effect on the shape and position of excitation and emission peaks, but has great effect on the intensity. When Er^{3+} concentration x = 0.01, the luminescence intensity of sample reaches the strongest, which is about 1.3 times of $Sr_{1.98}MgSi_2O_7:Eu^{2+}_{0.02}$; if x > 0.01, the luminescence intensity decreases with the increase of x. The possible reason is that there are some intermediate levels between the excited and ground state of Er^{3+}, which makes non-radiative energy transfer occur easily between each other. When the concentration of co-doped Er^{3+} increases, one part of Er^{3+} ions continue to transfer the energy to Eu^{2+}, while another part consume absorption energy in the form of non-radiative transitions, so the sensitization effect began to subside. Thus, the appropriate doping concentration (x) of Er^{3+} is x = 0.01 for $Sr_{1.98}MgSi_2O_7:Eu^{2+}_{0.02}$.

Effect of quantity of urea on luminescence properties of $Sr_{1.97}MgSi_2O_7:Eu^{2+}_{0.02}, Er^{3+}_{0.01}$: Combustion process is an exothermic reaction, which occurs with evaluation of light and heat. For any combustion process, reducer and oxidizer are required. In present system, nitrates were used as oxidizer and urea was employed as a reducer. The quantity of urea has great effect on heat output of combustion reaction and the intense level of combustion, furthermore decides self-propagating process of combustion reaction, the temperature of flame, which affects the formation of the sample and the temperature and time of post heat-processing[14]. Besides, urea can also provide reductive and protective atmosphere. It also can affect the valence state of rare earth ions in obtained phosphors. So the quantity of urea is an important factor for the luminescence properties of $Sr_{1.97}MgSi_2O_7:Eu^{2+}_{0.02}, Er^{3+}_{0.01}$. From Fig. 4, it can be seen that when R (R = the mass ratio of urea and nitrates) is 1.5:1, the luminescence intensity of $Sr_{1.97}MgSi_2O_7:Eu^{2+}_{0.02}, Er^{3+}_{0.01}$ is the highest. When R = 1:1, the intensity of emission peak is the lowest due to the incomplete combustion resulted from insufficient urea. When R = 2:1, the luminescence intensity of $Sr_{1.97}MgSi_2O_7:Eu^{2+}_{0.02}, Er^{3+}_{0.01}$ is also weaker than that with R = 1.5:1 and the apparent colour of phosphor shows a little dark. The main reason is that excessive urea resulted in a little carbon left in the sample, which makes the luminescence intensity decrease. So R = 1.5:1 is the optimum value of urea quantity.

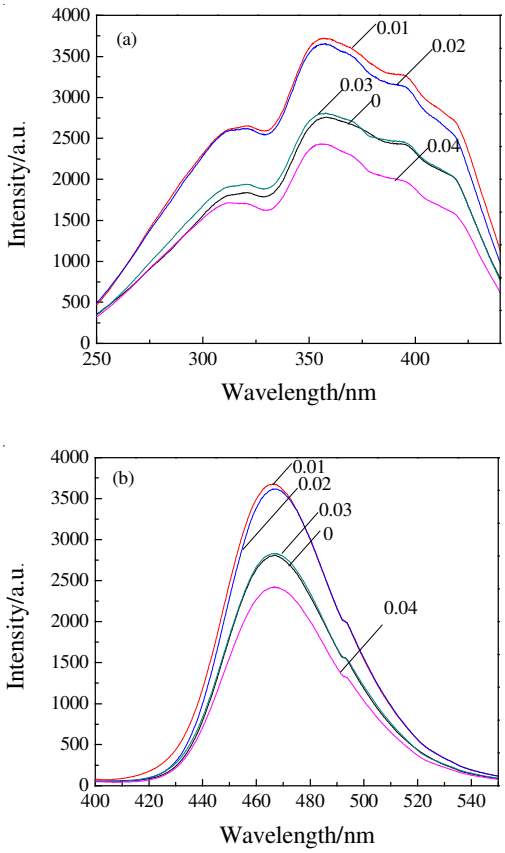

Fig. 3. Excitation spectra (a) and emission spectra (b) of $Sr_{1.98-x}MgSi_2O_7:Eu^{2+}_{0.02}, Er^{3+}_x$ (x = 0-0.04)

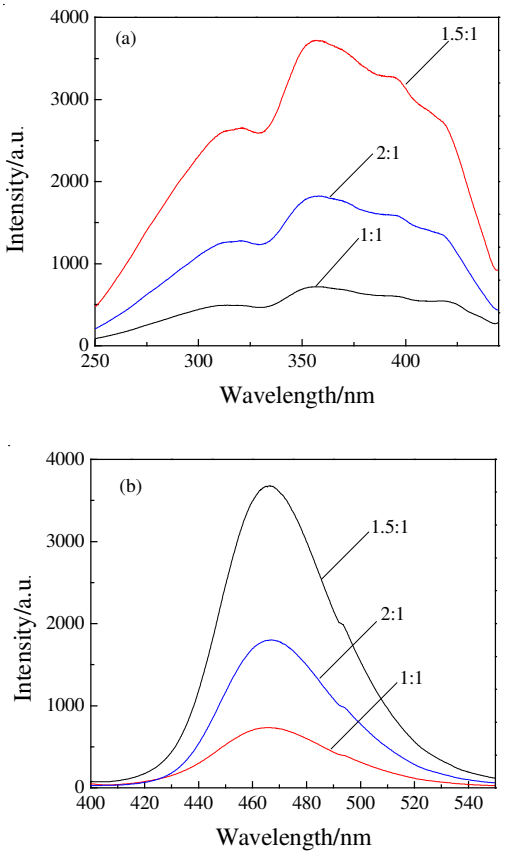

Fig. 4. Excitation spectra (a) and emission spectra (b) of $Sr_{1.97}MgSi_2O_7:Eu^{2+}_{0.02}, Er^{3+}_{0.01}$ phosphors at different quantity of urea (R)

Effect of dosage of flux H_3BO_3 on luminescence properties of $Sr_{1.97}MgSi_2O_7:Eu^{2+}_{0.02}$, $Er^{3+}_{0.01}$: Diffusion is one of the important processes affecting the rate of solid reaction. In general, proper flux is added into the system to decrease melting point and improve the diffusion rate. For luminescent materials, it is beneficial to the formation of the matrix, the doped ions entering into matrix lattice easily and improving luminescence intensity of products[15]. So, in our present work, H_3BO_3 was used as the flux and the effect of the dosage of H_3BO_3 on luminescence properties was investigated (while other conditions are fixed). It can be seen from Fig. 5 that the mole percent (y) of H_3BO_3 has little effect on the shape and position of excitation and emission peaks, but has great effect on their intensity. When H_3BO_3 mole percent y < 15 %, the emission intensity at 476 nm increases with the increase of y; the emission intensity is up to the highest when y = 15 %; if y > 15 %, the emission intensity begins to decrease significantly. The main reason is that excessive H_3BO_3 destroy the crystal structure of the host to some extent, which makes the luminescence efficiency of Eu^{2+} decrease. Therefore, it can be known that the appropriate amount of H_3BO_3 (y = 15 %) can improve luminescent intensity of the sample significantly.

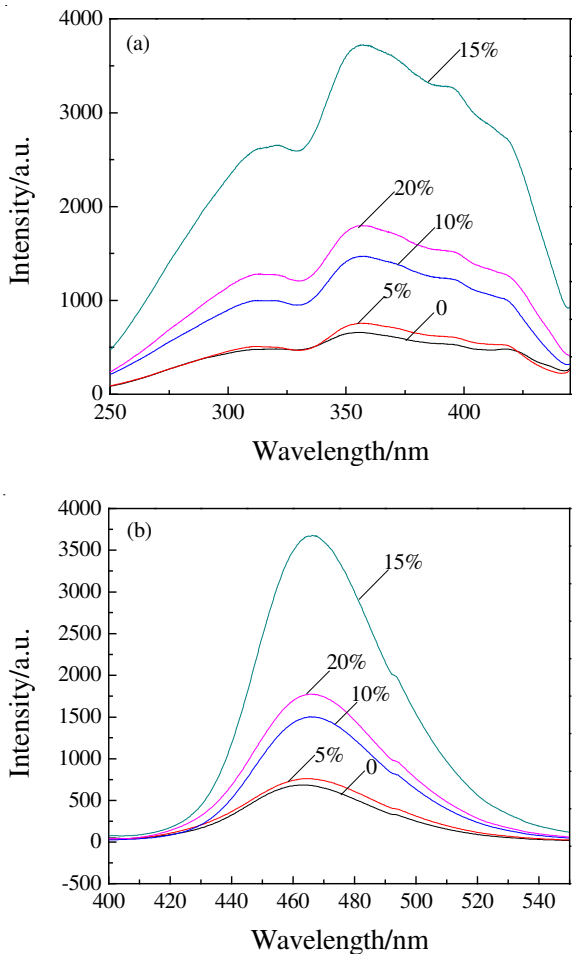

Fig. 5. Excitation spectra (a) and emission spectra (b) of $Sr_{1.97}MgSi_2O_7:Eu^{2+}_{0.02}$, $Er^{3+}_{0.01}$ at different dosage of H_3BO_3 (y = 0-20 %)

Conclusion

High-brightness blue emitting phosphors $Sr_2MgSi_2O_7:Eu^{2+}$, Er^{3+} were synthesized successfully by gel-combustion method assisted by microwave. This method has many advantages of low calcination temperature, short calcination time, weak reductive atmosphere, energy saving, easy operation, uniform composition and so on. The as-synthesized sample can be excited effectively by NUV-emitting LED chip due to their broad excitation band extending from 250-450 nm. Therefore, $Sr_2MgSi_2O_7:Eu^{2+}$, Er^{3+} shows good prospect for blue phosphors of white LED. Moreover, it is confirmed that the sample have the strongest luminescent bright when the concentration of co-doped Er^{3+} is 0.01, the mass ratio of urea and nitrate is 1.5:1 and the mole percent of boric acid is 15 %.

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