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Synthesis and Luminescent Characteristics of $BaGa_2S_4:Eu^{2+}$ Phosphor by Solid-state Method

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Abstract

Ⅱ-$Ⅲ_2$-$(S,Se)_4$ structured of phosphor have been used at various fields because they have high luminescent efficiency and broad emission band. Among these phosphors, europium doped $BaGa_2S_4$ was prepared by solid-state method. We investigated the possibility of applying [ ] due to emissive property of UV region. Also, general sulfide phosphors were synthesized by using injurious H_2S CS_2 gas. However, this study prepared $BaGa_2S_4:Eu^{2+}$ phosphor is addition to excess sulfur under 5% H_2/95% N_2 reduction atmosphere. So, this process could involved large scale synthesis because of non-harmfulness and simple process. The photo-luminescence efficiency of the prepared $BaGa_2S_4:Eu^{2+}$ phosphor increased by 20% compared with commercial $SrGa_2S_4:Eu^{2+}$ phosphor. From this, we could conclude that the prepared $BaGa_2S_4:Eu^{2+}$ could be applied to green phosphor for white LED of three wavelengths.

Keywords : $BaGa_2S_4:Eu^{2+}$, phosphor, LED

1. Introduction

The ternary compounds Ⅱ-$Ⅲ_2$-S_4 doped with Eu^{2+} are very attractive for lighting and display applications. Specially, $SrGa_2S_4:Eu^{2+}$ is well known as an efficient green-emitting phosphor, with excellent color coordinates (x=0.26, y=0.69) and high lumen equivalent (560 lm/W).

The existing $SrGa_2S_4:Eu^{2+}$ phosphors have been studied as a luminous device for CRT (Cathode Ray Tube), FED (Field Emission Display) and EL (Electroluminescence)[1-7]. This phosphor is also, under remarked for LED (Light Emitting Diode) phosphor, which make use of excitation characteristics of long wave region. This phosphor is prepared generally by conventional synthesis method using flux. However, this method requires high heat-treated temperature, long reaction time, complex process and harmful H_2S or CS_2 gas.

With this phosphor, we tried to substitute barium to strontium site and observed the properties of $BaGa_2S_4:Eu^{2+}$. Also, we have synthesized $BaGa_2S_4:Eu^{2+}$ phosphors using sulfide materials, and the mixture gas of 5 % H_2/95 % N_2 were used to avoid the H_2S or CS_2.

Peters and Baglio synthesized that under H_2S steam by $BaCO_3$, Ga_2O_3 and Eu_2O_3 in 1972[1]. However, this gas is very toxic to the human body and difficult to be treated if containated. Also, it has defects such as long reaction times and complicates process. Davolos attempted to synthesize the $BaGa_2S_4:Eu^{2+}$ at H_2S/Ar conditions from $BaCO_3$, Ga_2O_3 and Eu_2O_3 of high purity[8].

Accordingly, the purpose of this study is to make $BaGa_2S_4:Eu^{2+}$ with high luminescent efficiency by only first-firing treatment through an easy process and H_2S gas. Also, we manufactured white LED by using this phosphor. This shows it is possible to use, white LED lamp because of the high luminescent efficiency.

2. Experimental

In this study, we synthesized $Ba_{1-X}Ga_2S_4:Eu_X^{2+}$ ($0.001 \leq X < 0.3$) through typical solid-state method (Fig. 1). Starting materials were prepared were mainly sulfide materials, sulfide materials used calcium sulfide (BaS, 4N), gallium sulfide (Ga_2S_3, 4N) and europium sulfide (EuS, 3N).

First of all, raw materials were weighted, and then mixed at mortar. Then, it was dried in oven at 80 ℃ for a hour. This precursor was fired at 600~1100 ℃ in a tube

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furnace under 5 % H_2/95 % N_2 mixed gas atmosphere. The crystalline of phosphor powders were analyzed by XRD (X-ray Diffractometer, Rikaku DMAX-3) with Cu-Kα radiation and a Ni filter. Emission and excitation spectra of phosphor were obtained by Perkin Elmer LS50B luminescence spectrometer. Also, the phosphor size and shape were observed by SEM (Scanning Electron Microscopy, JEOL JSM6360).

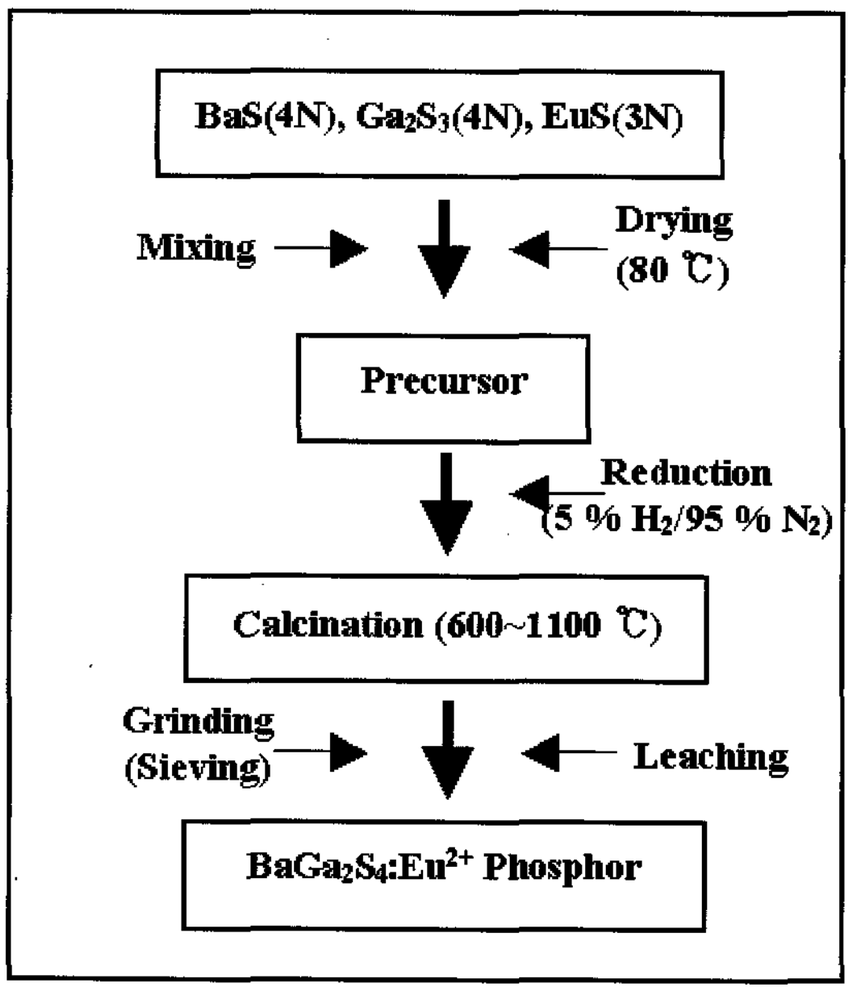


Fig. 1. Flow chart of experimental procedure.

3. Results

Fig. 2 shows typical PL excitation and emission spectra of $BaGa_2S_4:Eu^{2+}$ phosphor by solid-state reaction. Emission spectrum was measured under 405 nm excitation wavelength for UV white light LED. First of all, in the case of excitation spectrum, it has high excitation band in 300 nm~430 nm region which was emitted by various excitation sources. In the cases of emission band, main peaks appeared at 505 nm wavelength due to f-d energy transition of Eu^{2+} ion.

We expressed PL of $BaGa_2S_4:Eu^{2+}$ phosphor according to various firing temperature in Fig. 3. The phases slowly appeared at 700 ℃ and luminescent efficiencies enlarged as temperatures increases. In this figure, the best good luminescent intensity appears at 975 ℃. Phosphor particles are cohered together and decrease intensity in the temperature

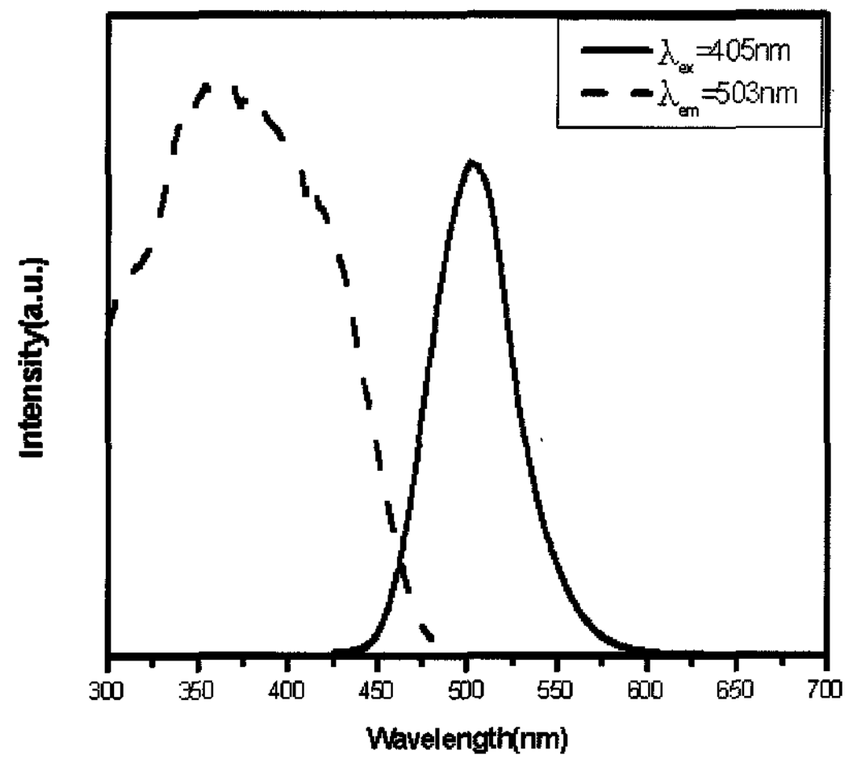


Fig. 2. Typical PL excitation and emission spectra of $BaGa_2S_4:Eu^{2+}$ phosphor prepared by solid-state reaction.

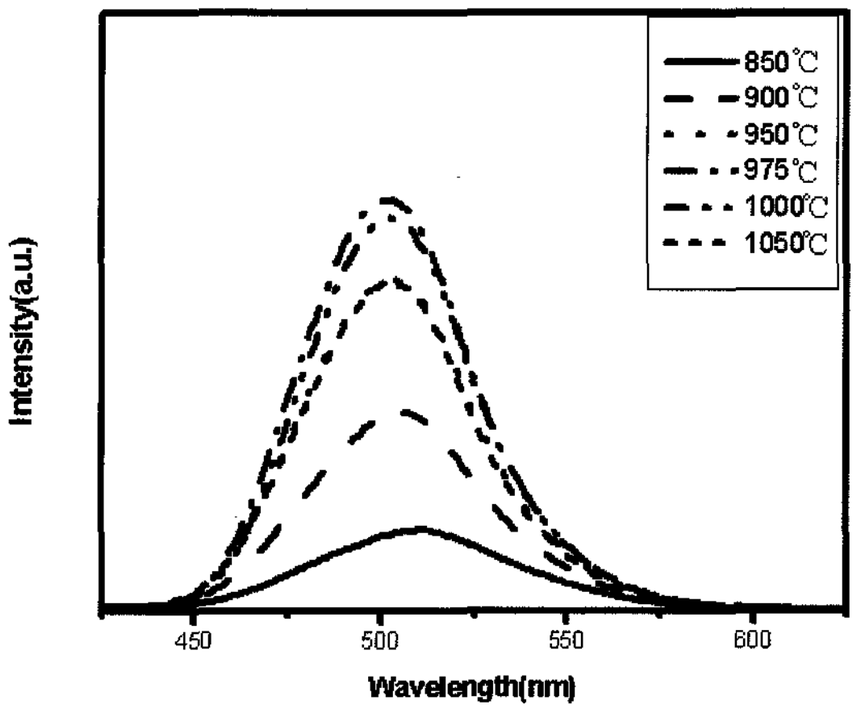


Fig. 3. PL emission spectra of $BaGa_2S_4:Eu^{2+}$ phosphors as a function of firing temperatures.

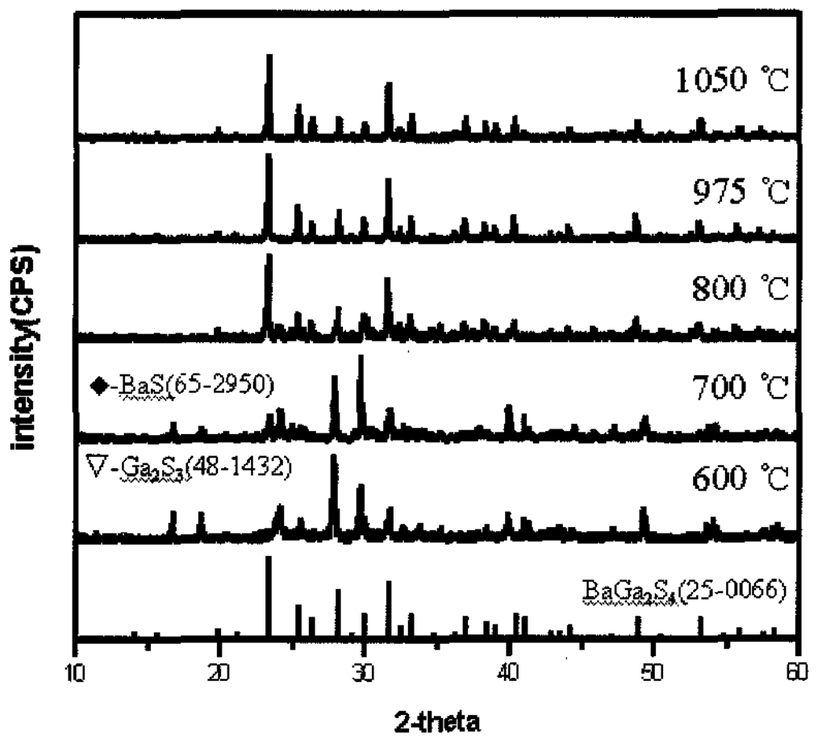


Fig. 4. XRD patterns of $CaGa_2S_4:Eu^{2+}$ synthesized at various temperature.

over 1000 ℃. It is a result of the temperature quenching phenomenon. The powder melted and then we observed glasses at over 1100 ℃ temperature.

In Fig. 4, we can confirm the crystalline of this through looking into the XRD patterns of $BaGa_2S_4:Eu^{2+}$ synthesized at various temperature. At 700 ℃, phosphor shows the $BaGa_2S_4$ (25-0066) phase. Powder are formed mainly at this phase where the temperature is 800 ℃ and shows the best crystalline at 1100 ℃.

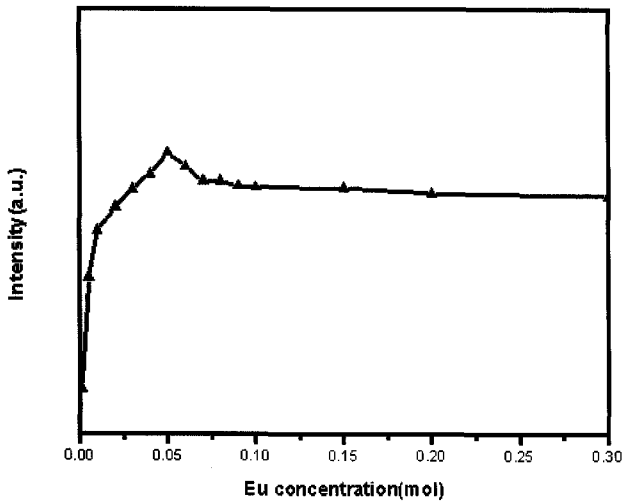
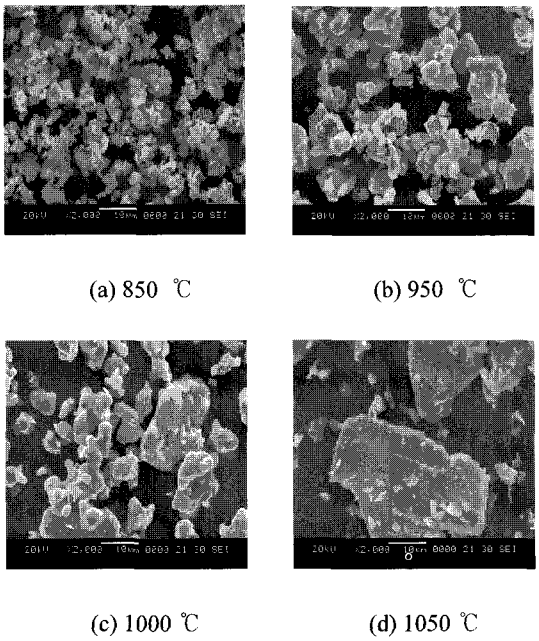


Fig. 5. PL emission intensities of $BaGa_2S_4:Eu^{2+}$ phosphors with respect to Eu^{2+} contents.

The changes of emission intensity at the various Eu^{2+} concentrations are depicted in Fig. 5. The most suitable doping concentration of Eu^{2+} was evaluated at 0.05 mole. The emission intensities decreased when over doped concentration of 0.05 mole Eu^{2+} ion because of concentration quenching. That is, emission of Eu^{2+} was absorbed another Eu^{2+} ion, because of the structural randomicity of phosphor and chemical complexity. Especially, increases of Eu^{2+} ion were cohered or converted killer[9].

Fig. 6 shows the morphology of $BaGa_2S_4:Eu^{2+}$ particles in the SEM image. At 850 ℃ in (a), particles have irregular shapes and it show particles growth as temperature increases. In (b) and (c), particles were formed uniform size of 5~10 ㎛. In case of (d), it shows cohesion phenomenon due to high thermal energy and material diffusion. The average size of this phosphor is under 10㎛. To apply the LED lamp, generally the most suitable size is



(a) 850 ℃ (b) 950 ℃

(c) 1000 ℃ (d) 1050 ℃

Fig. 6. SEM photographs of $BaGa_2S_4:Eu^{2+}$ phosphors in various firing temperature.

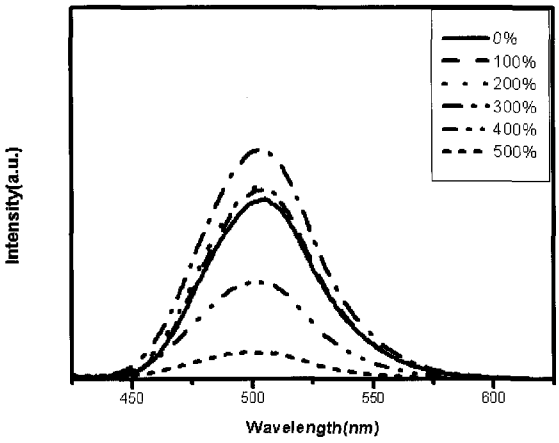


Fig. 7. PL emission spectra of $BaGa_2S_4:Eu^{2+}$ phosphors as a function of excessive sulfur.

the interior and exterior of 20 ㎛. Accordingly, powder of $BaGa_2S_4:Eu^{2+}$ can be used to LED lamp.

The synthesis of $BaGa_2S_4:Eu^{2+}$ correspond to the stoichiometry as starting materials, but sulfide materials have characteristic of easily volatilization. Accordingly, sulfur control is very important in this synthesis. Generally, it is synthesizes H_2S or CS_2 gas condition but it is very toxic and harmful. In this study, therefore, we attempted a simple process through 5 % H_2/95 % N_2 mixture gas and excess sulfur without H_2S gas.

In Fig. 7, PL emission spectra of $BaGa_2S_4:Eu^{2+}$ phosphors are shown as a function of excessive sulfur.

The luminescent efficiencies enlarged as sulfur percentage increased. In this figure, the highest luminescent intensity appears at excess 300 %. However, as sulfur addition exceed over 300 %, intensity of luminescence decreased because sulfur remain as not used reaction or not volatilized in phosphor decreased.

Fig. 8 displays relative PL emission spectra of synthesized phosphor and commercial $SrGa_2S_4:Eu^{2+}$ phosphor. Phosphor is proportional to the area as application of LED lamp. Hence, luminescent efficiency of [$BaGa_2S_4:Eu^{2+}$/ $SrGa_2S_4:Eu^{2+}$] is above 120 %.

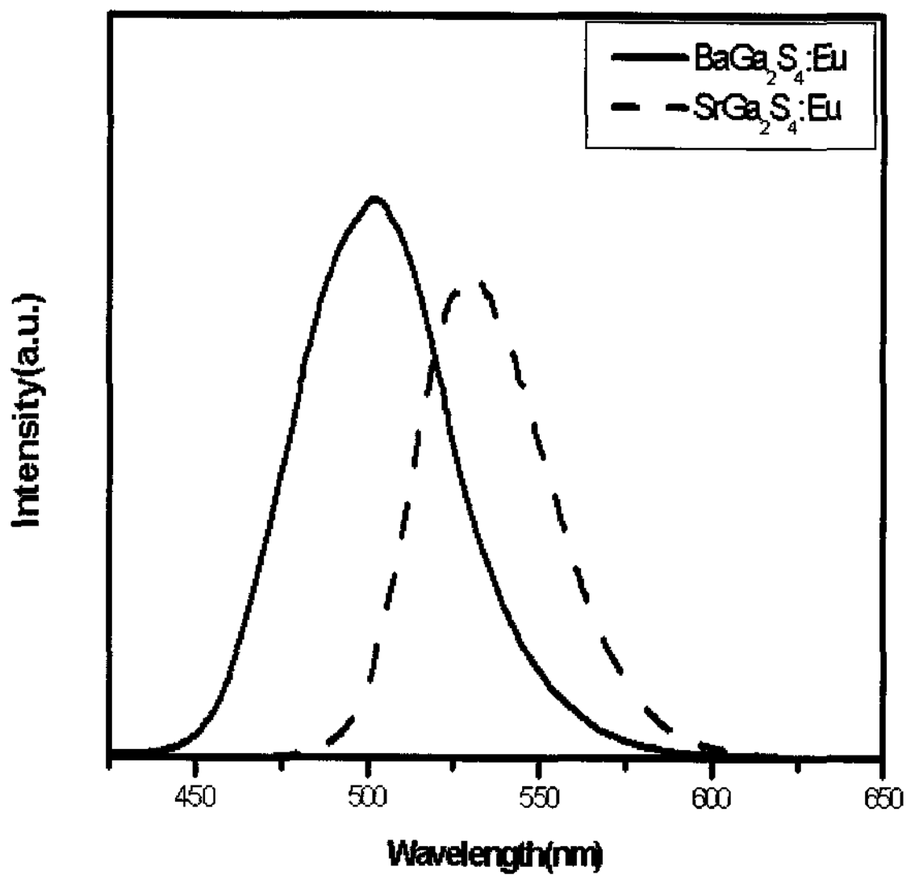


Fig. 8. Relative PL emission spectra of synthesized phosphor and $SrGa_2S_4:Eu^{2+}$ phosphor.

4. Conclusion

We obtained the best synthesis condition at 0.05 mole of Eu^{2+} concentration, under 100 cc/min reduction condition by adding excess 300 %/wt sulfur, at 975℃ heat-treated temperature and for 3 hours. It showed luminescent main peak of 505 nm and high excitation band in the range of 300 nm and 430 nm. Prepared phosphor showed higher luminescent efficiency of above 120 %. Consequently, $BaGa_2S_4:Eu^{2+}$ phosphor was confirmed to be applicable to the UV lamp for making LED lamp, and it can be applied for bluish green phosphor with excellent lumi-nescent efficiency.

5. References

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