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 field because those have high luminescent efficiency and broad emission band. Among these phosphors, europium doped $BaGa_2S_4$ was prepared by solid-state method and we try to look into an application possibility due to an 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 large scale synthesis because of non-harmfulness and simple process. The photo-luminescence efficiency of the prepared $BaGa_2S_4:Eu^{2+}$ phosphor increased 20% than commercial $SrGa_2S_4:Eu^{2+}$ phosphor. The prepared $BaGa_2S_4:Eu^{2+}$ could apply to green phosphor for white LED of three wavelengths.

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

Based on this phosphor, we tried to substitute barium to strontium site and that 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 at a human's body and difficult to be treated of it. Also it has defects such as long reaction times and complicates process. Davolos attempted the synthesis at H_2S/Ar conditions from $BaCO_3$, Ga_2O_3 and Eu_2O_3 of high purity[8].

Accordingly, in this study it has the purpose to make $BaGa_2S_4:Eu^{2+}$ with high luminescent efficiency by only first-firing treatment without a complex process and H_2S gas. Also, we manufactured white LED by using this phosphor. So, this shows possibility to be applicable for a 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≤X<0.3) through typical solid-state method (Fig. 1). Starting materials were prepared 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 are weighted, and then mixed at mortar. After it was dried in oven at 80 ℃ for a hour. This precursor was fired at 600~1100 ℃ in a tube 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 from

SEM (Scanning Electron Microscopy, JEOL JSM6360).

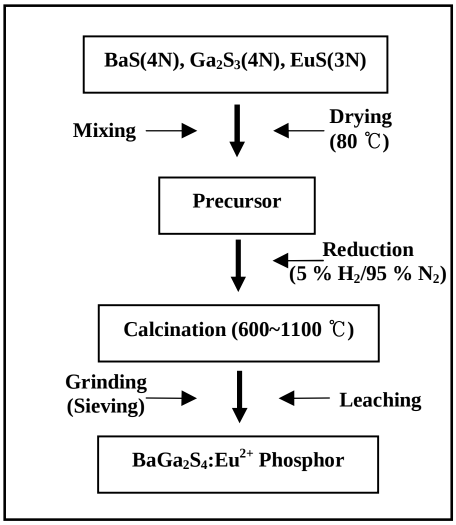


Fig. 1. Flow chart of experimental procedure.

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, case of excitation spectrum, it has high excitation band in 300 nm ~ 430 nm region which was emitted by various excitation sources. Cases of emission band, main peaks appear at 505nm wavelength due to f-d energy transition of Eu^{2+} ion.

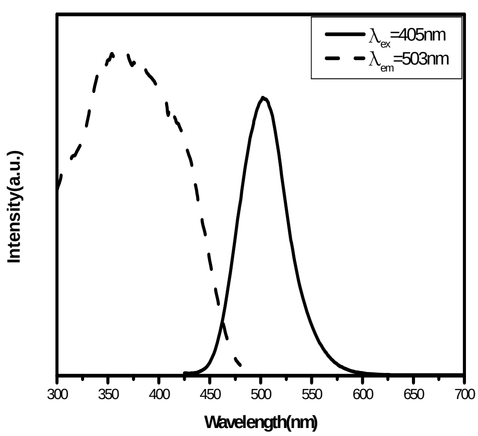


Fig. 2. Typical PL excitation and emission spectra of $BaGa_2S_4:Eu^{2+}$ phosphor prepared by solid-state reaction.

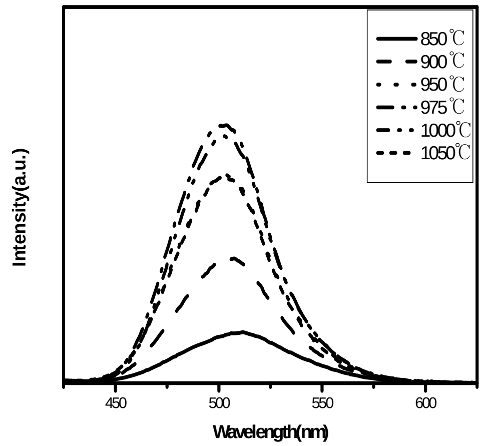


Fig. 3. PL emission spectra of $BaGa_2S_4:Eu^{2+}$ phosphors as a function of firing temperatures.

We expressed PL of $BaGa_2S_4:Eu^{2+}$ phosphor according to various firing temperature in Fig. 3. The phases are slowly appeared at 700 ℃ and luminescent efficiencies are enlarged as increasing temperatures. In figure, the best good luminescent intensity appears at 975 ℃. Phosphor particles are cohered together and decrease intensity in the temperature over that. It is a result of the temperature quenching phenomenon. And the powder was melted and then we observed glasses at over 1100 ℃ temperature.

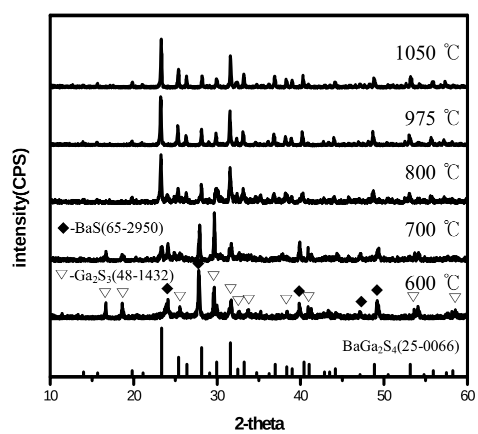


Fig. 4. XRD patterns of $CaGa_2S_4:Eu^{2+}$ synthesized at various temperature.

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 has the $BaGa_2S_4$ (25-0066) phase. Powder are formed mainly phase of this at 800 ℃ and show a best good crystalline at 1100 ℃.

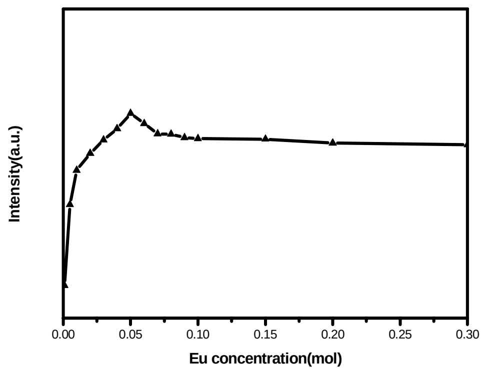
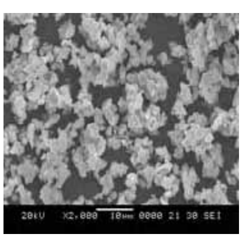
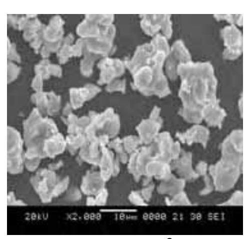


Fig. 5. PL emission intensities of $BaGa_2S_4:Eu^{2+}$ phosphors with respect to Eu^{2+} contents.

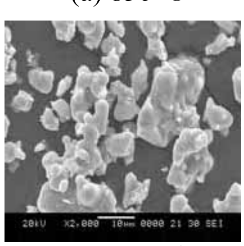
The changes of emission intensity are depicted in Fig. 5 on the various Eu^{2+} concentrations. The best suitable doping concentration of Eu^{2+} was evaluated 0.05 mole. The emission intensities are decreased when over doped concentration of 0.05 mole Eu^{2+} ion because of concentration quenching.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



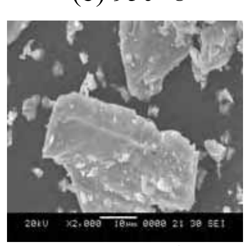
(a) 850 ℃



(b) 950 ℃



(c) 1000 ℃



(d) 1050 ℃

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

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 increasing temperature. In (b) and (c), particles were formed uniform size of 5~10 ㎛. In case of (d), it display cohesion phenomenon due to high thermal energy and material diffusion. Average size of this phosphor is under 10 ㎛. For applying the LED lamp, generally best size is the interior and exterior of 20 ㎛. Accordingly powder of $BaGa_2S_4:Eu^{2+}$ can be used to LED lamp.

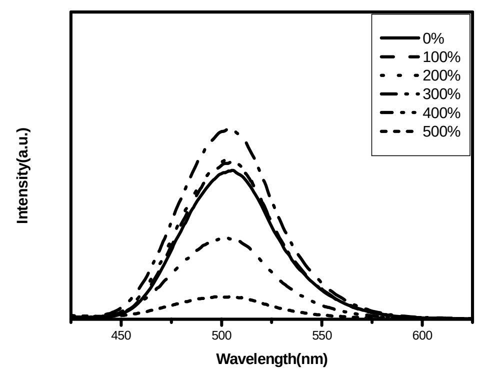


Fig. 7. PL emission spectra of $BaGa_2S_4:Eu^{2+}$ phosphors as a function of excessive sulfur.

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 synthesis. Generally it was synthesized H_2S or CS_2 gas condition but it is very toxic and harmful. And in this study, we attempted simply 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 show as a function of excessive sulfur. The luminescent efficiencies are enlarged as increasing sulfur percentage. In figure, the best good luminescent intensity appears at excess 300 %. However, as over 300 % excessive sulfur addition decrease intensity because sulfur remain as not used reaction or not volatilized in phosphor.

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%.

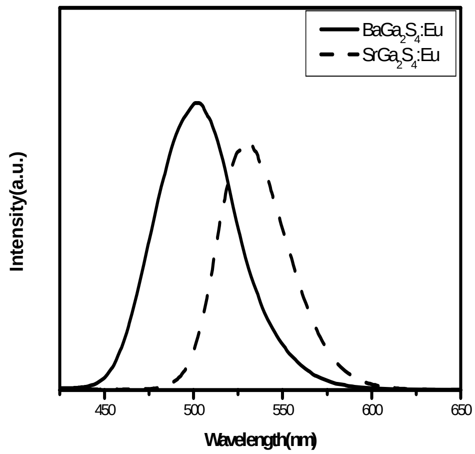


Fig. 8. Relative PL emission spectra of synthesized phosphor and $SrGa_2S_4:Eu^{2+}$ phosphor.

4. Conclusion

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

5. References

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