Synthesis of the $CaGa_2S_4:Eu^{2+}$ phosphors and Application in White LEDs

***Jae Myung Kim**, Kyung Nam Kim, Joung Kyu Park, Chang Hae Kim and Ho Gyeom Jang* [*]

Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejon 305-600, Korea

[*]Department of Chemistry, Korea University Anam-dong Sungbuk-ku, Seoul, 136-701, Korea.

. hypnosis@krict.re.kr

Abstract

The thiogallate phosphors which are well known for a long time as phosphor materials for CRT or EL device were reported. Those have high luminescent properties at long-wavelength region. Among those phosphors, the samples with divalent europium doped $CaGa_2S_4$ were prepared by a simple process under the reduction atmosphere (5% H_2/ 95% N_2) without toxic gas such as H_2S or CS_2. The prepared phosphor shows a higher luminescent efficiency (about 120%) than that of $YAG:Ce^{3+}$ phosphor. Consequently, this phosphor is possible to be applicable to white LED lamp because of the high luminescent efficiency.

1. Introduction

LED succeeded Laser light known for the miracle materials at 21 centuries as a next generation display light device. The semiconductor materials composed of Ⅲ-ⅤA have emission efficiency of about 100% and operate at high temperature. Those are used to electronic devices because of easy electronic transitions. LEDs was developed for high power chips (InGaN, GaN) at Nichia a corporation in 1993 that could be utilized at the illumination and display.[1] Specially, a combination of YAG:Ce yellow phosphor and blue chip chiefly makes white LEDs for illuminations.[2~3]

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).[4~6]

Based on this phosphor, we tried to substitute calcium to strontium site and that observed the properties of $CaGa_2S_4:Eu^{2+}$.

Peters and Baglio synthesized that under H_2S steam by $CaCO_3$, Ga_2O_3 and Eu_2O_3 in 1972.[4] However this gas is very toxic at a human's body and difficult to be treated of it. Aidaev attempted the synthesis at low temperature from NH_4CNS but it has defects such as long reaction times and complicates process.[7]

Accordingly, in this study it has the purpose to make $CaGa_2S_4:Eu^{2+}$ 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 $CaGa_2S_4:Eu^{2+}$ through typical solid-state method. Starting materials were prepared mainly sulfide materials, sulfide materials used calcium sulfide (CaS, 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 600~900℃ in a tube furnace under 5% H_2/95% N_2 mixed gas atmosphere. The crystalline of phosphor powders were analyzed by XRD (Rikaku DMAX-3) with Cu-K α 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 (JEOL JSM6360).

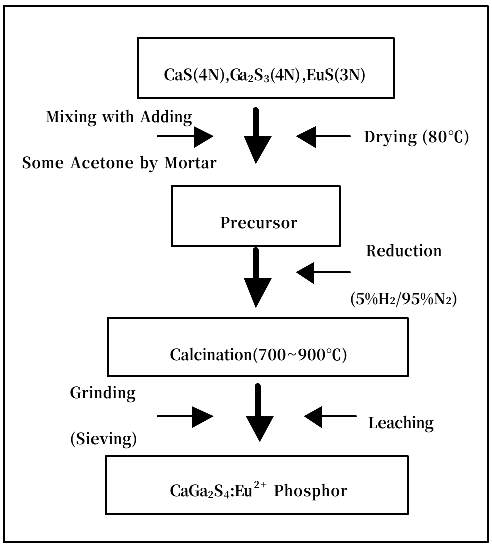

Fig. 1 Flow chart of experimental procedure.

3. Results and discussion

Fig. 2 shows typical PL excitation and emission spectra of $CaGa_2S_4:Eu^{2+}$ phosphor by solid-state reaction. Emission spectra were measured under 405nm and 465nm excitation wavelength because it has been used to GaN and InGaN chip for white light LEDs. First of all, in a case of excitation spectrum, that has high excitation band at 380nm ~ 550nm region. On occasion of emission band, main peaks are appeared at 553nm wavelength due to f-d energy transition of Eu^{2+} ion.

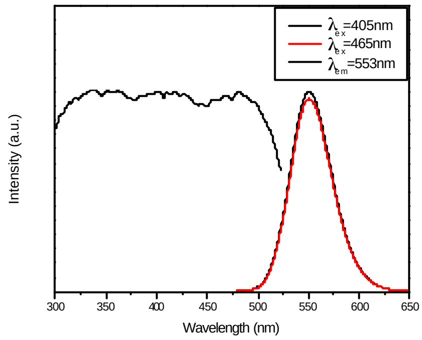

Fig. 2 Typical PL excitation and emission spectra of $CaGa_2S_4:Eu^{2+}$ phosphor prepared by solid-state reaction.

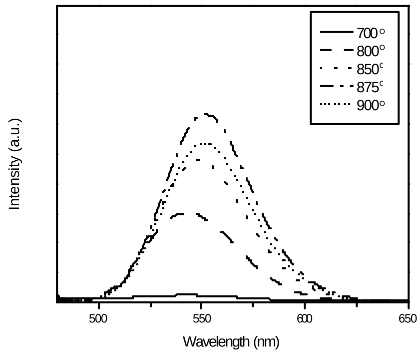

Fig. 3 PL emission spectra of $CaGa_2S_4:Eu^{2+}$ phosphors as a function of firing temperatures.

We expressed PL of $CaGa_2S_4:Eu^{2+}$ 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 875℃. 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 925℃ temperature.

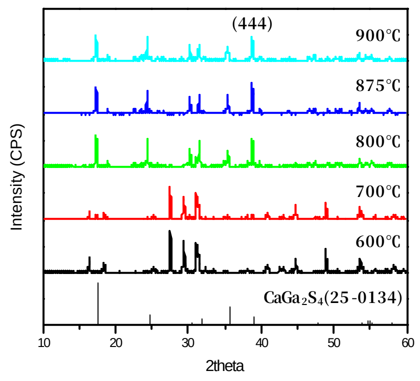

Fig. 4 XRD patterns of $CaGa_2S_4:Eu^{2+}$ synthesized at various temperature

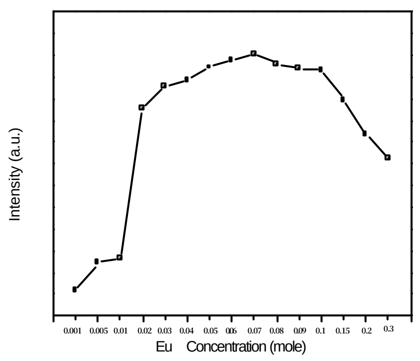

Fig. 5 PL emission intensities of $CaGa_2S_4:Eu^{2+}$ phosphors with respect to Eu^{2+} contents. (λ_{ex}=465nm)

We can confirm the crystalline of this through looking into the XRD patterns of $CaGa_2S_4:Eu^{2+}$ synthesized at various temperature. At 700℃, phosphor has the $CaGa_2S_4$ (25-0134) phase. Powder are formed mainly phase of this at 800℃ and show a best good crystalline at 875℃. Also at over 900℃, total crystalline dropped and (444) plane displayed large diminution.

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 0.07mole. The emission intensities are decreased when over doped concentration of 0.07 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.[8]

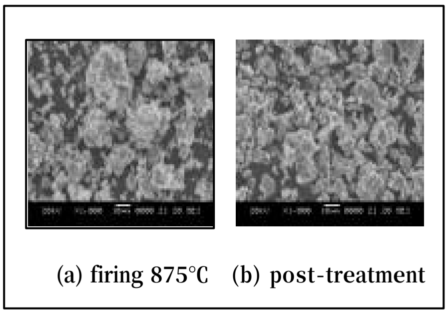

Fig. 6 SEM photographs of $CaGa_2S_4:Eu^{2+}$ phosphors.

Fig. 6 shows the morphology of $CaGa_2S_4:Eu^{2+}$ particles in the SEM image. Average size of this phosphor is under 20㎛. For applying the LED lamp, generally best size is the interior and exterior of 10㎛. Accordingly powder of $CaGa_2S_4:Eu^{2+}$ can be used to LED lamp. And through a post-treatment process $CaGa_2S_4:Eu^{2+}$ phosphors appear small and fixed size. Also post-treatment process has improved in luminescent efficiency of PL. (Fig.7) It was explained that phosphor which has narrow distribution reduced light scattering of energy transition.

Finally, Fig. 8 compares $CaGa_2S_4:Eu^{2+}$ phosphor with commercial $YAG:Ce^{3+}$ phosphor. Luminescent efficiency of [$CaGa_2S_4:Eu^{2+}$/$YAG:Ce^{3+}$] has over 120% and at a aspect of luminescent intensity it is about 200%. But it needs still many supplementations for white LED lamp. Color purity has falloff than YAG and sulfide phosphors must have coating process because of implantation of chip.

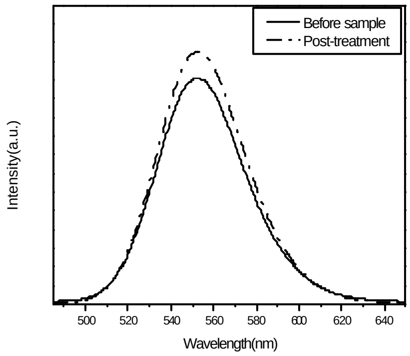

Fig. 7 PL emission spectra of $CaGa_2S_4:Eu^{2+}$ phosphor before sample and post-treatment process. (λ_{ex}=465nm)

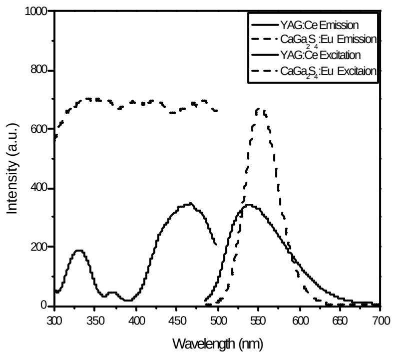

Fig. 8 Relative PL emission spectra of synthesized phosphor and YAG:Ce^{3+} phosphor. (λ_{ex}=465nm)

4. Conclusion

$CaGa_2S_4:Eu^{2+}$ phosphor was prepared by solid state method through using raw materials of sulfide compounds without H_2S gas. When we obtained the best synthesis condition at 0.07 mole of Eu^{2+} concentration, under 100cc/min reduction condition, at 875℃ heat-treated temperature and for 3 hours. Prepared phosphor shows higher luminescent efficiency with above 120% than that of YAG:Ce^{3+} phosphor. And we can confirm the possibility to be applied to yellow phosphor for white LEDs.

5. References

[1] S. Nakamura and G. Fasol, *Springer. Berlin.*, 343(1997)

[2] Y. Narukawa et al, *Jpn. J. Appl. Phys.*, **41**, 371(2002)

[3] R. Mueller-Mach and G. O. Mueller, *Proc. SPIE.*, **3938**, 30(2000)

[4] T. E. Peters, J. A. Baglio, *J. Electrochem. Soc.*, **119,** 230(1972).

[5] S. Yang et al, *Appl. Phys. Lett.*, **72**, 158(1998).

[6] P. Benalloul, C. Barthou and J. Benoit, *J. Alloy Compd.*, **275-277**, 709(1998)

[7] F. Sh. Aidaev, *Inorg. Mater.*, **39**, 96(2003).

[8] H. W. Laverenz, *Dover, New York.*, 333-337(1968)