# Preparation and Optical Properties of $SrGa_2S_4$:Eu Phosphor

**Young Rag Do,* Jae Woo Bae, Youhyuk Kim,† and Hong-Geun Yang**

*Samsung Display Devices Co. LTD, 575 Shin-dong, Suwon-si, Kyunggi-do 442-391, Korea*
*†School of Fundamental Sciences, Dankook University, Cheonan, Chungnam 330-714, Korea*
*Received May 10, 1999*

The photoluminescence and cathodoluminescence of $SrGa_2S_4$:Eu phosphor were optimized with the process and chemical variables (activators, fluxes and reaction temperature) used in solid state reaction. Firing the powder with flux at 800 °C for 2hr gave the highest photoluminescence efficiency under near-UV excitation and the highest cathodoluminescence efficiency of 20.1 lm/W at 2 kV and 33.3 lm/W at 10 kV. The suitability of $SrGa_2S_4$:Eu for application as a phosphor in LCDs and FEDs is discussed.

## Introduction

Field Emission Display (FED) is at the very forefront of thin flat-panel display. It is one of the main priorities of the FED area to find and develop phosphors which show high luminescent efficiency under low-energy e-beam excitation (<5 kV). The principal operating parameters of a FED, namely the duty cycle, the anode operating voltage, and the peak current density, affect the selection of a FED phosphor.[1,2] In particular, compared to 10 in a CRT, FED has a longer pixel address time of 30 $\mu$s. Stoffer *et al.* suggest that the long dwell time has led to the concept of activator recycling.[2,3] Fast activators can be excited and reemit light many times during the long dwell time of 30 $\mu$s. Activator recycling would only be possible if the dwell time is longer than the activator decay time. It has been suggested that sulfide phosphors activated either by trivalent cerium or divalent europium would be viable candidates for FED application, because $SrGa_2S_4$:Eu and $SrGa_2S_4$:Ce, Na have allowed transition and a short decay time. For this reason, $SrGa_2S_4$:Eu phosphor was studied in several papers for low voltage cathodoluminescence applications.[3-7] These papers elucidated that thiogallate phosphors demonstrate superior chromaticity, intrinsic efficiency, aging properties and saturation behavior. Even though the excellent cathodoluminescence (CL) properties of $SrGa_2S_4$:Eu phosphor were studied, there is insufficient evidence to support a theory that the preparation variables used in the flux aided solid state reaction. The first objective of this work is to optimize CL properties with the process and chemical variables (activators, fluxes and reaction temperature) used in the solid state reaction of $SrGa_2S_4$:Eu phosphor for the application of FED.

In addition to CL application, $SrGa_2S_4$:Eu phosphor has shown the strong potential of green phosphor in a new device application such as phosphor emitting LCD. Our lab recommended a new application of photoluminescence (PL) phosphors to front-emitting LCD in which a color filter can be replaced with phosphors in a color LCD.[8] The first requirement of this application is that phosphors have a higher PL efficiency in the near UV-Violet region, such as 350-420 nm.[8-10] A previous report indicated that $SrGa_2S_4$:Eu phosphor has a strong excitation peak in the range of 300-450 nm.[11] The second objective of this study is to investigate the detailed PL properties according to preparation conditions and to measure the quantum efficiency of $SrGa_2S_4$:Eu phosphor under UV-violet excitation. Therefore, an investigation into its optical properties, cathodoluminescence emission and decay property according to the process variable was carried out to determine its suitability for use in FEDs or phosphor LCDs.

## Experimental Section

$SrGa_2S_4$:Eu phosphor was prepared by a solid state reaction method with or without flux. The starting materials were $SrCO_3$, $Ga_2O_3$ and the activator was introduced as $Eu_2O_3$. The starting materials were weighed out in stoichiometric quantities, and they were ground together in a mortar and pestle, and introduced onto an alumina crucible in a horizontal tube furnace. The appropriate amounts of NaBr were utilized as a flux to decrease reaction temperature and calcination time. The mixtures were calcined at 600, 700, 800, 900 and 1000 °C for 2 hours in a flowing $H_2S$ stream. The $H_2S$ was replaced by Ar to prevent the oxidation of the mixture when the temperature of the mixtures receded below 500 °C during the initial and final processing stages. The resultant products were removed from the furnace in the shape of sintered cakes. The phosphor cake was then mortared, washed and sieved prior to evaluation. X-ray diffraction patterns of powdered phosphors were obtained using a Phillips model PW1800 X-ray diffractometer with $CuK_\alpha$ radiation. Diffraction patterns were taken over the range of $20° < 2\theta < 80°$ with a scan rate of $1°2\theta$/minute. PL properties were measured from the exciting deep powder patches under UV excitation. Excitation and photoluminescence measurements were carried out using a 0.275 m triple grating monochromator with an Acton Research Co. PHV400 photomultiplier tube, and the excitation source was a 500 W Xe-lamp. The incident beam is perpendicular to the surface of the sample, and the observation angle is equal to 45° with normal to excitation source. The quantum efficiency of PL emission was measured in the integrating sphere under UV-violet excitation. Cathodoluminescence measurements were investigated in the high vacuum ($1\times10^{-6}$ torr) chamber

under various levels of excitation energy. For the measurement of CL properties, samples were prepared using settled (potassium silicate binder) screens on indium-tin oxide glass. Phosphor-coated glass slides were placed in a demountable cathode ray tube and excited with an electron beam pulsed with various frequency. The luminance was measured on the same side. Decay time measurements under cathode-ray excitation were carried out with a pulsed beam under the following conditions: pulse duration, 0.01 $\mu$s; frequency, 72 Hz; accelerating voltage, 2.0 kV; current density 10$\mu$A/cm$^2$. The light output was analyzed by a PHV400 photomultiplier tube, and a Hewlett Packard 54600A oscilloscope. SEM pictures of resultant powders were measured using a JEOL Model JSM-5300 microscope. SEM pictures of powders were used for the assessment of particle shape and particle sizes qualitatively. The size distribution of phosphor powder was analyzed by using a Particle Data Inc. model 130XY SM Coulter counter.

## Results and Discussion

Polycrystalline samples of $Sr_{1-x}Ga_2S_4:Eu_x$ ($x$=0.005-0.05) powders were prepared by a high temperature solid state reaction with or without the aid of flux. The composition of $Sr_{1-x}Ga_2S_4:Eu_x$ ($x$=0.005-0.05) compounds are nominal value. In order to determine the crystallization behavior of specimens fired with or without the aid of flux, the phases formed at different temperatures were identified by powder XRD (Figure 1). It shows that the structure of $SrGa_2S_4$:Eu phosphor is an orthorhombic $PbGa_2Se_4$ structure.[12,13] When the firing temperature is increased, no peak shift is observed, which indicates that no change occurs in the lattice parameter. Even though it is anticipated that by increasing the firing temperature Eu ion would be incorporated completely into the $SrGa_2S_4$ lattice, the cell parameter of $SrGa_2S_4$ (a=20.840, b=20.495, c=12.212 Å) is similar to that of $EuGa_2S_4$ (a=20.716, b=20.404, c=12.200 Å).[12,13] When the solid state reaction was performed with a flux such as NaBr, polycrystalline strontium thiogallates were formed below 600°C and completed crystallization at 800 °C. The crystallization was retarded in the case of non-flux synthesis. The X-ray intensity of the main diffraction peaks increased in the presence of flux. Also, Figure 2 demonstrates that the full width at half-maximum (FWHM) of the (422) diffraction peaks of the particles fired with NaBr is smaller than that of particles fired without flux. This indicates that $SrGa_2S_4$:Eu particles fired with flux exhibit a higher crystallinity than those fired without flux. The data from the Coulter counter show the size distribution and mean particle size of phosphor powders obtained from a solid state reaction with NaBr (Figure 3). The particle size distribution of $SrGa_2S_4$:Eu particles exhibited a single peak with a median value of 6 $\mu$m. Figure 4 shows the morphology of $SrGa_2S_4$:Eu particles in the SEM image. It is apparent from the SEM image that the size of particles fired with NaBr is larger than that of particles fired without flux. XRD, Coulter counter and SEM data indicate that a small amount of flux is required to grow the well-crystallized crystals of $SrGa_2S_4$:Eu particles. Also, they indicate that the particle size and shape of $SrGa_2S_4$:Eu phosphor are suitable to be utilized in the application of the screening process in display devices.

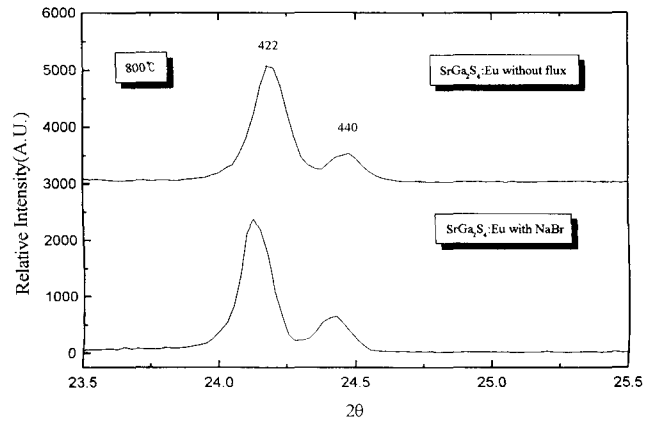


**Figure 2.** The full width at half-maximum (FWHM) of the (422 diffraction peaks.

Figure 5 shows the emission spectrum of two kinds of $SrGa_2S_4$:Eu (2 atom % Eu) phosphors obtained from firing with or without flux. The green emission band in the emission spectrum consists of the usual 5d→ 4f band.[14] It indi-

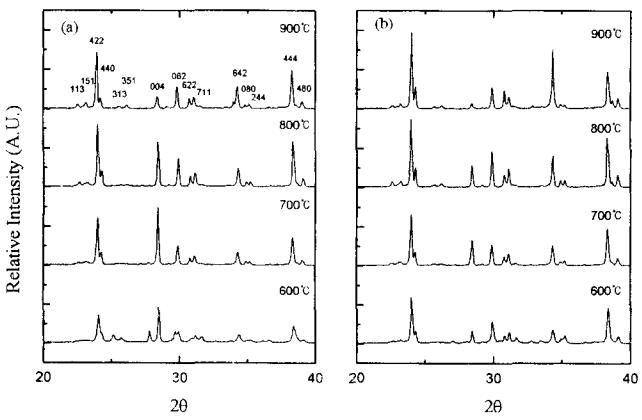


**Figure 1.** X-ray diffraction patterns of $SrGa_2S_4$:Eu crystals fired at different temperatures (a) without flux (b) with NaBr.

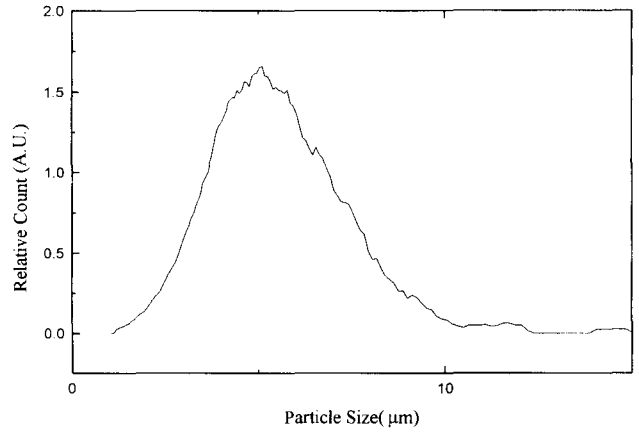


**Figure 3.** The size distribution of $SrGa_2S_4$:Eu crystals fired with NaBr at 800 °C for 2hr.

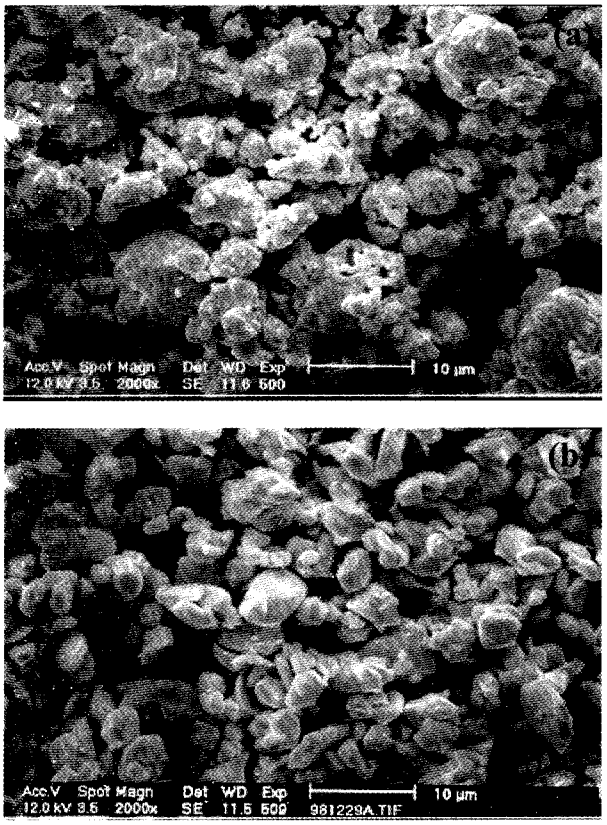


**Figure 4**. SEM images of $SrGa_2S_4$:Eu crystals fired (a) without flux (b) with NaBr at 800 °C for 2hr.

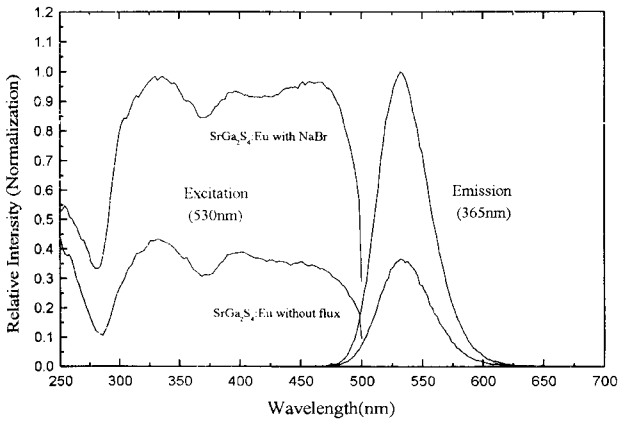


**Figure 5**. Excitation spectra ($\lambda_{em}$=530 nm) and photoluminescence spectra ($\lambda_{ex}$=365 nm) of $SrGa_2S_4$:Eu crystals fired at 800 °C for 2hr.

cates that the $SrGa_2S_4$:Eu phosphor obtained from the flux-aided solid state reaction has a much stronger emission peak in the green region under 365 nm excitation than the phosphor from a non-flux reaction. The higher luminescent intensity is a result of the better crystallinity of $SrGa_2S_4$:Eu phosphor fired with flux. This behavior has usually been observed in phosphor synthesis. Figure 6 shows the relationship between the photo-luminescent intensity of the phosphor particles (fired at 800 °C for 2h with NaBr) and the atomic concentration of Eu ion dopants. The intensity reaches a maximum at a doping concentration of 2 atom %

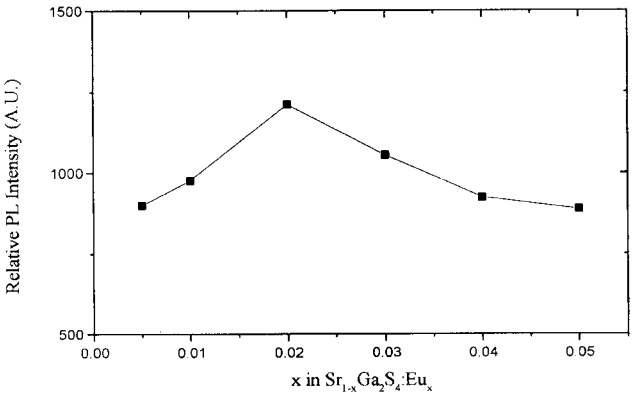


**Figure 6**. Relative photoluminescence intensity ($\lambda_{ex}$=365 nm) of $SrGa_2S_4$:Eu powders as a function of the atomic concentration o Eu ion in $SrGa_2S_4$:Eu phosphor.

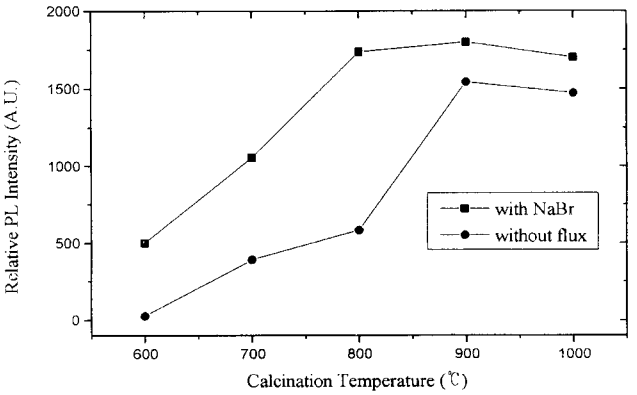


**Figure 7**. Relative photoluminescence intensity ($\lambda_{ex}$=365 nm) of $SrGa_2S_4$:Eu powders as a function of the firing temperature.

Eu ion, but excess Eu doping decreases the intensity. Therefore, 2 atom % of Eu ion is the optimum concentration for the best photo-luminescent intensity in our experiment. Figure 7 indicates that the particles fired at a higher temperature produce higher emission intensity. Maximum PL intensity is obtained from particles fired with flux at 800°C and without flux at 900 °C. These results are in complete agreement with the crystallography results. Also the efficiency of the particles at higher temperature is higher than that of the particles fired at lower temperature, because of the higher crystallinity and less surface area of the particles at higher temperature. The excitation spectrum of $SrGa_2S_4$:Eu (2 atom % Eu) phosphor is shown in Figure 5. The excitation spectrum extends into visible region and overlaps the emission band to a considerable extent. The broad band in the visible region is due to $Eu^{2+}$ absorption. As previously reported, the $Sr^{2+}$ site of $SrGa_2S_4$:Eu phosphor, which has a $PbGa_2Se_4$ structure, is surrounded by 8 anions in a distorted arrangement. The broad excitation band of $Eu^{2+}$ in $SrGa_2S_4$ results from an overlap between three excitation bands which are generated by the transition between $4f^7$ and the lowest three levels of the $5d^1$ state.

In the general color LCDs, the white light source on the rear side and the color filters arranged on each pixel on the front side are simply combined. Usually, LCD shows a nar-

row viewing angle and reduced brightness because it is a passive emitting display device and it is based on the switching of polarized light. Several publications[8-10] have suggested that phosphor emitting LCD could be obtained by combining a UV light source and UV-exciting phosphor layers, in order to enlarge the viewing angle and to increase the brightness of LCDs. The strong, broad excitation band of $SrGa_2S_4$:Eu phosphor between 350-420 nm suggests that it can be a promising candidate for the phosphor LCD application. The quantum efficiency of photoluminescence was measured in the integrating sphere under UV-violet excitation to check the possibility of $SrGa_2S_4$:Eu for phosphor LCD application. The detailed measurement technique is presented elsewhere.[5] Quantum efficiency($\eta$) can be obtained from the following equation:

$$\eta = \frac{\int \lambda \cdot P(\lambda) d\lambda}{\int \lambda \cdot \{E(\lambda) - R(\lambda)\}(\lambda) d\lambda}$$

where $P(\lambda)$ is the emission spectrum, $E(\lambda)$ is the excitation spectrum, and $R(\lambda)$ is the reflectance spectrum. Table 1 summarizes the quantum efficiency of the $SrGa_2S_4$:Eu phosphor under 388 nm and 394 nm. Previous publications[8,9] suggested that both $CaSO_4$:Eu and $SrMgP_2O_7$:Eu phosphors could be used as a backlight phosphor in the phosphor-LCD, since they have a strong emission peak in the near UV-violet wavelength range. The emitting wavelength of $CaSO_4$:Eu is 388 nm and that of $SrMgP_2O_7$:Eu is 394 nm. The quantum efficiency of $SrGa_2S_4$:Eu phosphor fired with NaBr is 0.55 at 388 nm and 0.57 at 394 nm. The CIE chromaticity coordinates of the room temperature PL of $SrGa_2S_4$:Eu and ZnS:CuAl are shown in Figure 8. For $SrGa_2S_4$:Eu (2 atom % Eu), the color coordinates are x=0.270, y=0.685 and compared with the ZnS:CuAl powder data measured in our lab using high voltage cathodoluminescence (25 kV). The color coordinates are x=0.280, y=610 for ZnS:CuAl. Table 2 lists the CIE chromaticity coordinates measured as a function of europium concentration in $SrGa_2S_4$ powder under 394 nm excitation. The chromaticity coordinates of the $SrGa_2S_4$:Eu green-emitting powders under UV excitation are insensitive to the europium activator concentration in a range from 0.5 to 5.0 atom %. Thus, it is clearly observed that $SrGa_2S_4$:Eu phosphor provides a more saturated green than the CRT green phosphor whose color coordinates correspond to a yellow-green color. The purer green emission of $SrGa_2S_4$:Eu fired with NaBr is considered to be an extremely efficient for phosphor LCD application.

Another interesting characteristic of $SrGa_2S_4$:Eu investigated in this work is the cathodoluminescence of $SrGa_2S_4$:Eu under low voltage (< 5 kV) excitation. The cathodoluminescence spectrum is shown in Figure 9. It shows that the $SrGa_2S_4$:Eu phosphor obtained from the flux-aided solid state reaction has a much stronger emission peak in the green region under e-beam excitation than the phosphor from a non-flux reaction. Brightness data were converted into intrinsic efficiency ($\eta$) with respect to electron beam energy according to the formula:

$$\eta(lm/W) = \frac{100\pi L_0}{jV}$$

where $L_0$ is the brightness in cd/m$^2$, $j$ is the electron beam

**Table 1**. The quantum efficiency of $SrGa_2S_4$:Eu phosphor fired at 800 °C for 2hr

| Phosphors | 365 nm excitation | 388 nm excitation | 394 nm excitation |
|---|---|---|---|
| $SrGa_2S_4$:Eu fired with NaBr | 0.53 | 0.55 | 0.57 |
| $SrGa_2S_4$:Eu fired without flux | 0.19 | 0.22 | 0.23 |

**Table 2**. The CIE chromaticity coordinates of $Sr_{1-x}Ga_2S_4:Eu_x$ (x=0.005-0.05)

| x in $Sr_{1-x}Ga_2S_4:Eu_x$ | 394 nm UV excitation color coordinates; x, y | Electron beam excitation (2 kV) color coordinates; x, y |
|---|---|---|
| 0.005 | 0.265, 0.687 | 0.260, 0.693 |
| 0.01 | 0.267, 0.686 | 0.258, 0.694 |
| 0.02 | 0.270, 0.685 | 0.265, 0.688 |
| 0.03 | 0.271, 0.684 | 0.264, 0.689 |
| 0.04 | 0.272, 0.684 | 0.258, 0.696 |
| 0.05 | 0.271, 0.684 | 0.260, 0.693 |

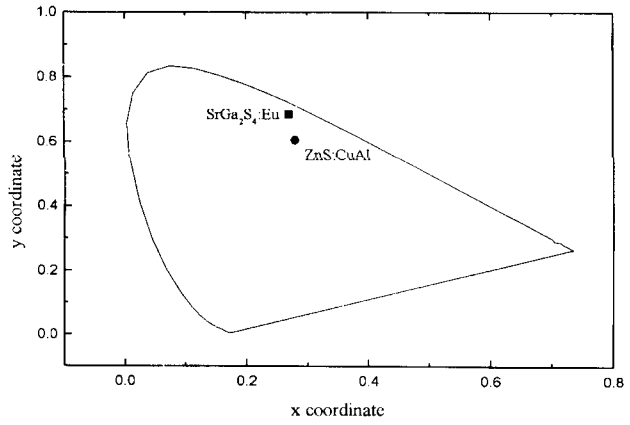


**Figure 8**. Comparisons of the CIE chromaticity coordinates o $SrGa_2S_4$:Eu (2 atom % Eu) and commercial ZnS:CuAl.

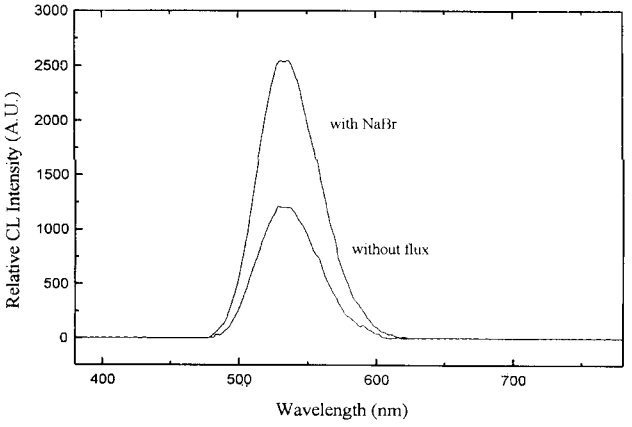


**Figure 9**. Catholuminescence spectra of $SrGa_2S_4$:Eu crystals fired at 800 °C for 2hr.

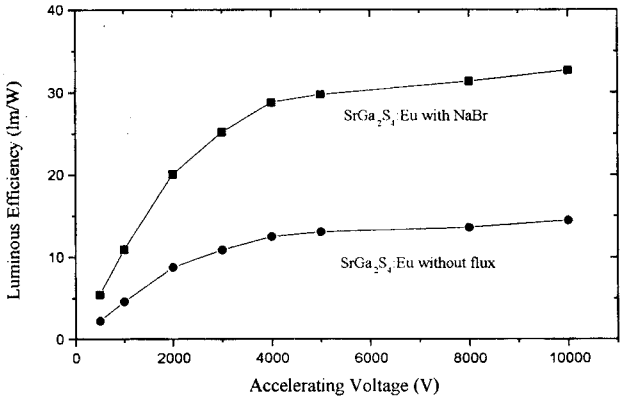


**Figure 10**. Luminous efficiencies of $SrGa_2S_4$:Eu phosphors as a function of excitation voltage (current density 10$\mu$A/cm$^2$).

current density in $\mu$A/cm$^2$, and V is the accelerating voltage in volts. Figure 10 shows the dependence of the efficiency of the two kinds of $SrGa_2S_4$:Eu (2 atom %) phosphors, which are prepared with NaBr and without flux, on the applied voltage under the following conditions: pulse duration, 30 $\mu$s; frequency, 72 Hz; current density 10 $\mu$A/cm$^2$. Figure 9 and Figure 10 also make it clear that a flux-aided reaction provides a better phosphor from the view point of cathodoluminescence efficiency. The relationship between intrinsic efficiency and applied voltage also demonstrated that the $Eu^{2+}$ activated $SrGa_2S_4$ phosphors exhibit an intense cathodoluminescence response in the high voltage area. Table 2 also indicates that a change in Eu concentration in a range from 0.5 to 5.0 atom % does not affect the chromaticity coordinates under CL excitation. As with the PL results, the chromaticity coordinates of $SrGa_2S_4$:Eu are excellent for green phosphor and indicate that the color of this phosphor is purer than that of the commercially available green phosphor in CRT. The decay curve of $SrGa_2S_4$:Eu phosphor is obtained at 300K with the decay time (10% decay) of approximately 2.5 $\mu$s. The short decay time of $SrGa_2S_4$:Eu phosphor is in agreement with the previous report,[1,2] where the d-f transition of $Eu^{2+}$ activator is spin allowed and parity allowed. The fast decay time of $SrGa_2S_4$:Eu phosphor has the advantage of minimizing the effect of phosphor saturation due to ground state depletion.[3,4] The decay curve also confirms that $SrGa_2S_4$:Eu phosphor is a suitable candidate for green emitting phosphor in a FED device.

## Conclusion

In summary, we present the photoluminescence and cathodoluminescence of $SrGa_2S_4$:Eu phosphors obtained from a solid state reaction with or without flux. PL efficiency, CL output, chromaticity coordinates and decay time suggest that $SrGa_2S_4$:Eu phosphor will be a candidate for green phosphor in LCDs and FEDs. Experimental results obtained from different preparation conditions indicate an optimum Eu concentration of 2 atom percent and an appropriate firing temperature of 800-900 °C. Also, flux-aided solid state reaction provides a suitable method of preparing a mass produced and efficient $SrGa_2S_4$:Eu phosphor.

**Acknowledgment**. This work was supported by the research program of Samsung Display Devices.

## References

1. Yang, S.; Zhang, F.; Stoffers, C.; Jacobsen, S. M.; Summers, C. J.; Yocom, P. J.; McClelland, S. *Proc. SPIE* **1998**, *194*, 2408.
2. Stoffers, C.; Yang, S.; Jacobsen, S. M.; Summers, C. J. *J. SID* **1996**, *4*, 337.
3. Stoffers, C.; Yang, S.; Zhang, F.; Jacobsen, S. M.; Wagner, B. K.; Summers, C. J. *Appl. Phys. Lett.* **1997**, *71*(13), 1759.
4. Yang, S.; Stoffers, C.; Zhang, F.; Jacobsen, S. M.; Wagner, B. K.; Summers, C. J. *Appl. Phys. Lett.* **1998**, *72*(2), 158.
5. Yang, S.; Stoffers, C.; Zhang, F.; Wagner, B. K.; Penczek, J.; Jacobsen, S. M.; Summers, C. *J. Euro. Display '96* **1996**, 81.
6. Jacobsen, S. M. *J. Soc. Informa. Display* **1996**, *4*, 331.
7. Ronot-Limousin, I.; Garcia, A.; Fouassier, C.; Barthou, C.; Benalloul, P.; Benoit, J. *J. Electrochem. Soc.* **1997**, *144*, 687.
8. Do, Y. R.; You, Y. C.; Jeong, J. Y.; You, Y. C. *US Patent* 5608554, 1997.
9. Newport, A. C.; Vecht, A.; Bayley, P. A.; Crossland, W. A. *SID98 Digest* **1998**, 239.
10. Crossland, W. A.; Springle, I. D.; Davey, A. B. *SID97 Digest* **1997**, 837.
11. Natarajan, B. R.; Conway, J.; Mueller-Mach, R.; Mueller, G.O. *The Fourth International Conference on the Science and Technology of Display Phosphors* **1998**, 369.
12. Peters, T. E.; Baglio, J. A. *J. Electrochem. Soc.* **1972**, *119*, 230.
13. Eisenmann, B.; Jakowski, M.; Klee, W.; Schäfer, H. *Rev. Chim. minér.* **1983**, *20*, 255.
14. Davolos, M. R.; Garcia, A.; Fouassier, C.; Hagenmuller, P. *J. of Solid State Chem.* **1989**, *83*, 316.
15. Do, Y. R. unpublished paper (in press).