Cathodoluminescent properties of rare-earthe-doped $SrGa_2S_4$ thin film phosphors excited with low energy electrons

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Abstract

The deposition of $SrGa_2S_4$ thin film phosphors doped with Ce or Eu aiming at application for FEDs has been carried out by a multi-source deposition technique. A $SrGa_2S_4$ phase was formed by annealing process and $SrGa_2S_4$ thin films which were deposited using a Ga_2S_3/Sr flux ratio larger than 50 and annealed in H_2S showed luminance and luminous efficiency of about 1700 cd/m^2 and 2.95 lm/W, respectively, with (0.13, 0.10) chromaticity in the activation with Ce, and about 4000 cd/m^2 and 7.05 lm/W, respectively, with (0.36, 0.60) under excitation with 3 kV and 60•A/cm^2. The results obtained this experiment demonstrate the potential of $SrGa_2S_4$ thin film phosphors for FED screens.

1. Introduction

Field emission displays (FEDs) are one of the future flat-panel display technologies [1,2]. They operate at low voltage excitation (1-5 kV). At the low voltage excitation, the phosphors which are used in CRTs can not show high luminance and efficiency in FEDs because of their high resistivity [3]. Therefore,, phosphors must have low resistivity to suppress the charging-up, moreover, they must have stable surface for high-density electron beam irradiation io order to suppress deterioration. One of the methods to overcome these problems is use of a thin film as phosphor layer, because thin film phosphors are expected to have advantages such as low electrical resistance in the direction along thickness, decrease of surface areas, high resolution and contrast.

Ce- or Eu-doped $SrGa_2S_4$ phosphor powder is well known as one of the potential candidates for a blue or green emitting phosphor, respectively, due to its high luminous efficiency, saturated chromaticity and stability [4]. $SrGa_2S_4$ contains Sr-S and Ga-S bonds and each binding energy is significantly different. With regard to prepare this ternary compound thin film, molecular beam epitaxy (MBE) [5] and multi-source deposition (MSD) [6] techniques were widely employed. In this investigation, we are reporting our work on the structural and luminescent properties of $SrGa_2S_4$ thin film phosphors doped with Ce or Eu prepared by multi-source deposition technique.

2. Experimental

$SrGa_2S_4$ thin film phosphors doped with Ce or Eu were deposited on quartz glass substrates using Sr metal, Ga_2S_3 and RCl_3 (R = Ce, Eu) powders as evaporation sources by multi-source deposition technique, where Ga_2S_3 to Sr flux ratio were 2.5, 6.7 and 50 in the case of $SrGa_2S_4$:Eu, and 60 in the case of $SrGa_2S_4$:Ce, a substrate temperature (T_S) was 450•€, and film thickness was about 500 nm. After the deposition, the films were annealed at 800•€ for several terms in H_2S flow diluted with Ar (H_2S : Ar = 1 : 100).

Structural properties of the films were characterized by X-Ray diffraction (XRD) curves and Auger electron spectroscopy (AES). The luminescent properties of the films characterized by

325 nm of He-Cd laser and electron beam of energy lower than 3 kV, respectively at room temperature.

3. Results and discussion

3.1 Structural properties of $SrGa_2S_4$ thin films

Figure 1 shows XRD curves of the $SrGa_2S_4$:Ce thin films as-deposited and annealed in H_2S atmosphere, where the films were deposited at Ga_2S_3/Sr flux ratio of about 60. It can be seen that as-deposited film shows only GaS {002} phases. On the other hand, the film annealed at 800•€ for 15, 30, 45 and 60 min in H_2S shows $SrGa_2S_4$ diffraction peaks. This result shows that Sr atoms exist as amorphous in the as-deposited films and that annealing process induces reactions between Sr, GaS and S_2, leading to the growth of a $SrGa_2S_4$ phase. Nearly the same results were obtained also in the case of $SrGa_2S_4$:Eu, although the Ga_2S_3/Sr flow rate was 50.

It was found from AES measurement that although about 10 at% of oxygen exist in the as-deposited film, the oxygen contents decrease to lower than 1 at% by the annealing in H_2S.

3.2 Luminescent properties of $SrGa_2S_4$:Eu thin films

Figure 2 shows dependence of CL spectra of the annealed films on Ga_2S_3/Sr flux ratio, where the anode voltage (V_a) and sample current density (J_S) were kept at 2 kV and 60 •A/cm^2, respectively.

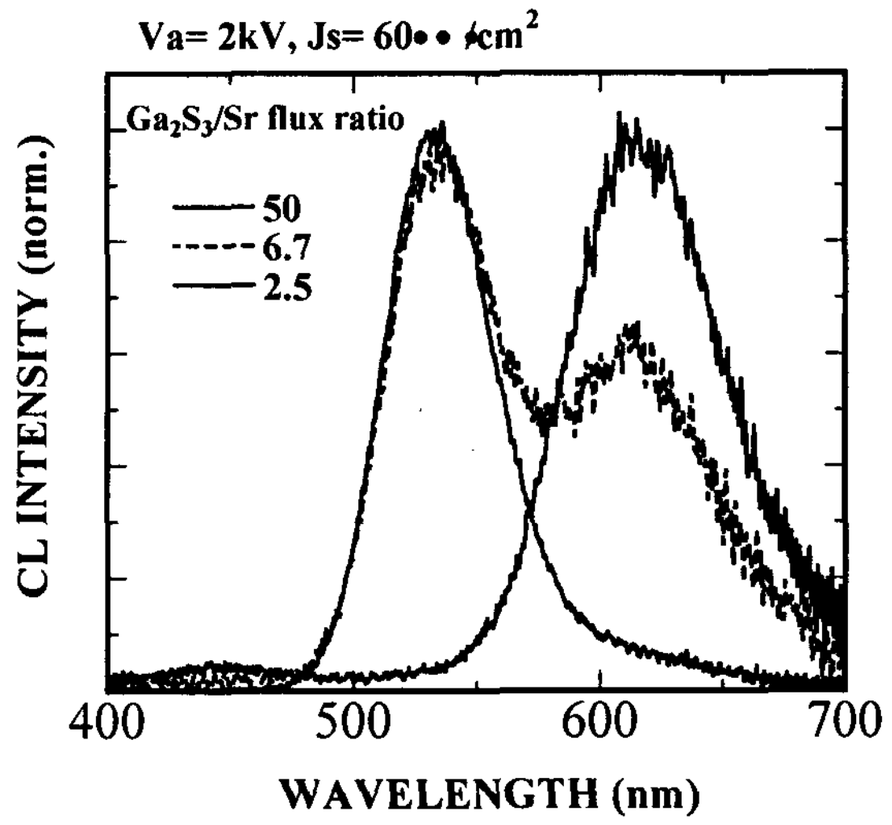

Fig.2 Dependence of CL spectra of $SrGa_2S_4$:Eu thin films annealed at 800°C for 1 h in H_2S on Ga_2S_3/Sr flux ratio.

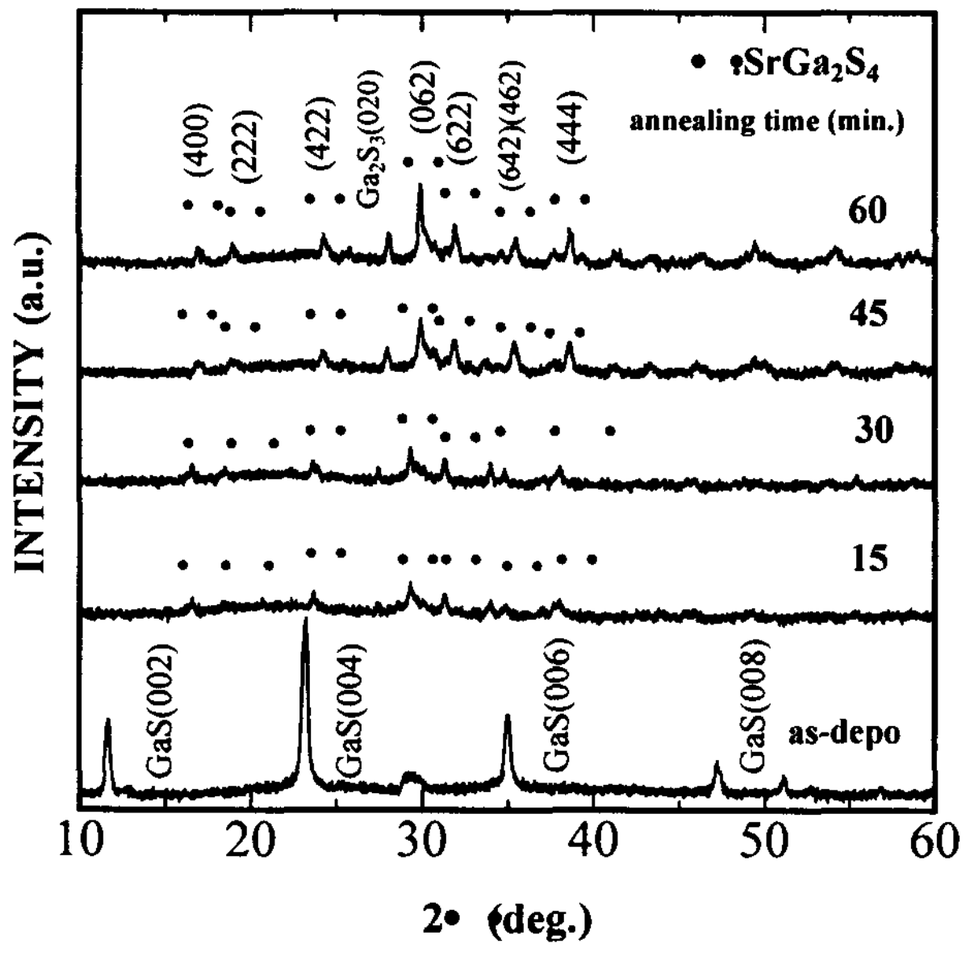

Fig.1 XRD curves of $SrGa_2S_4$:Ce thin films deposited at 450°C, which annealed at 800°C in H_2S atmosphere.

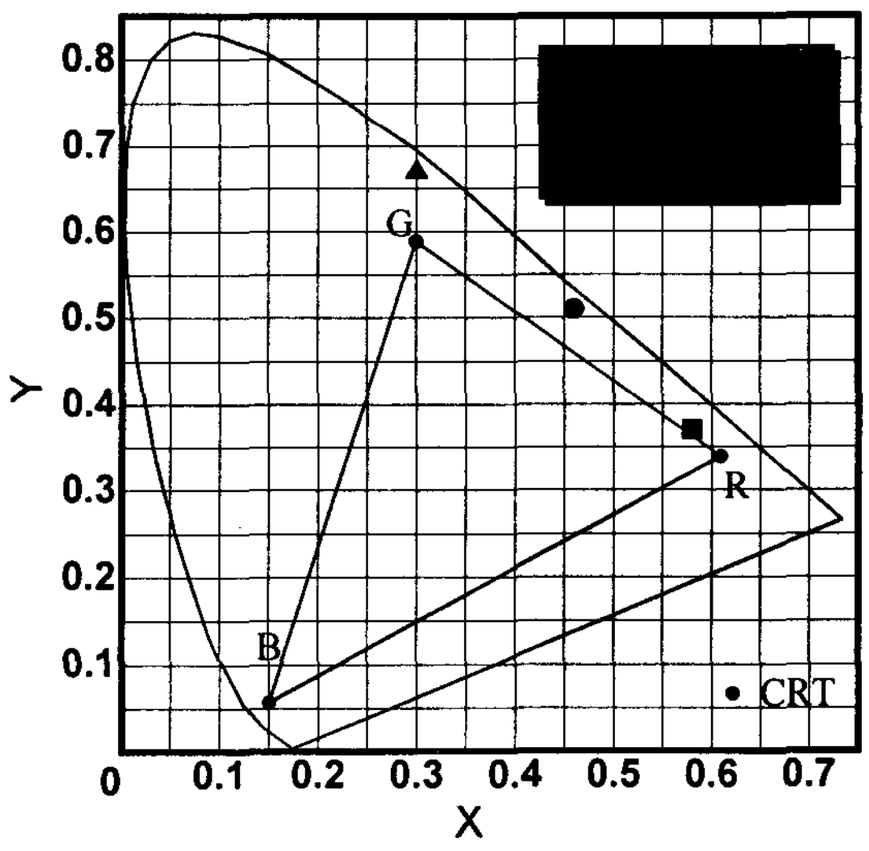

Fig.3 CIE color coordinates of the spectra shown in Fig.2.

Figure 3 shows CIE color coordinates of the spectra shown in Fig.2. It can be seen that the film deposited at a flux ratio of 50 shows only green emission with color coordinates of (0.30, 0.67) due to Eu^{2+} ion in the crystal field of $SrGa_2S_4$. However, the color coordinates of the films deposited at flux ratios of 2.5 and 6.7 shift toward red region, because the emissions from these films contain red component due to SrS:Eu as shown in Fig.2. The reason which the CIE color coordinates shift to red when the Ga_2S_3/Sr flux ratio decreases is thought to be as follows. Electron beam at 2 kV excite only the surface of the film, because the penetration depth of the beam is shallow (< 50 nm) [7]. Therefore, the fact that red emission due to SrS:Eu is contained at low flux ratio means that compositional fraction of Ga and S at the surface region are small. This deficiency is thought to be caused by re-evaporation of GaS from the film during the annealing, whereas at the flux ratio of 50, the lack of GaS at the surface region is supplied by the diffusion from the inner region of the film. Figure 4 shows the luminance and efficiency of the $SrGa_2S_4$:Eu films as a function of V_a, where J_S = 60• A/cm^2. It can be seen from the results that the luminance and efficiency of the films prepared at a G_2S_3/Sr flux ratio of 50 are about 500 cd/m^2 and 3.3 lm/W at V_a = 1 kV, respectively, moreover when the anode voltage is up to 3 kV, the luminance and efficiency become about 4000 cd/m^2 and 7.05 lm/W, respectively.

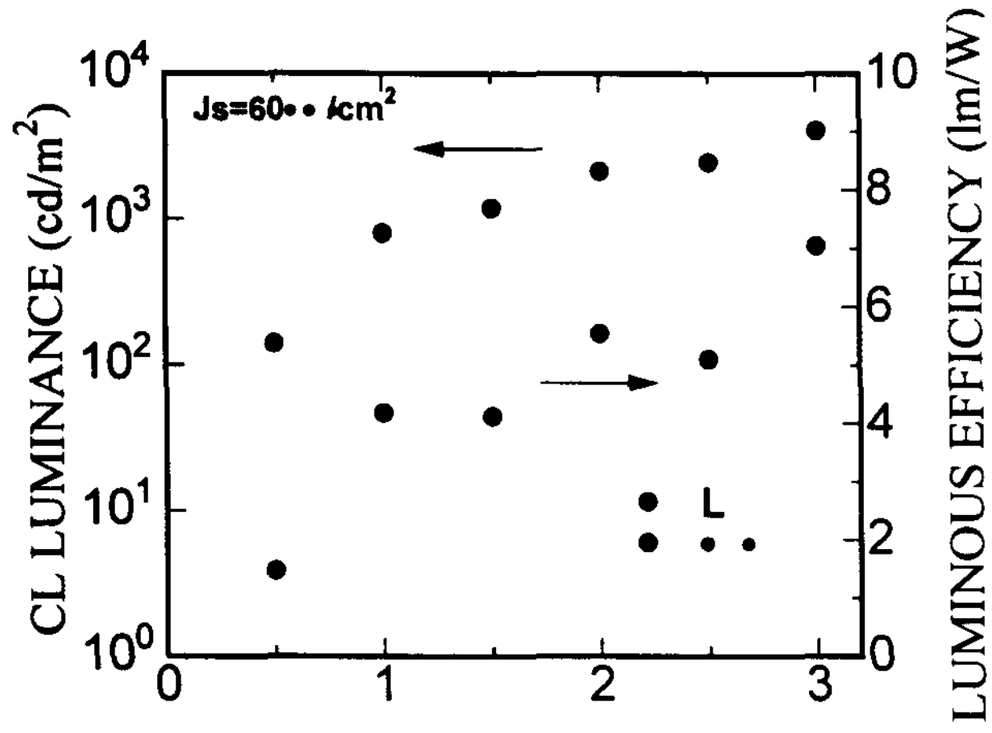

Fig.4 CL luminance and luminous efficiency of $SrGa_2S_4$:E thin film deposited at 450°C and annealed at 800°C in H_2S atmosphere.

3.3 Luminescent properties of $SrGa_2S_4$:Ce thin films

Figure 5 shows PL spectra of the $SrGa_2S_4$:Ce thin films deposited at the flux ratio of about 60, and annealed for 15, 30, 45 and 60 min in H_2S atmosphere. These were excited with 325 nm of He-Cd laser. All of the films show a main emission with a peak at 445 nm and a sub emission with a peak at 490 nm, which are attributed to the emission due to inner transition in Ce^{3+}.

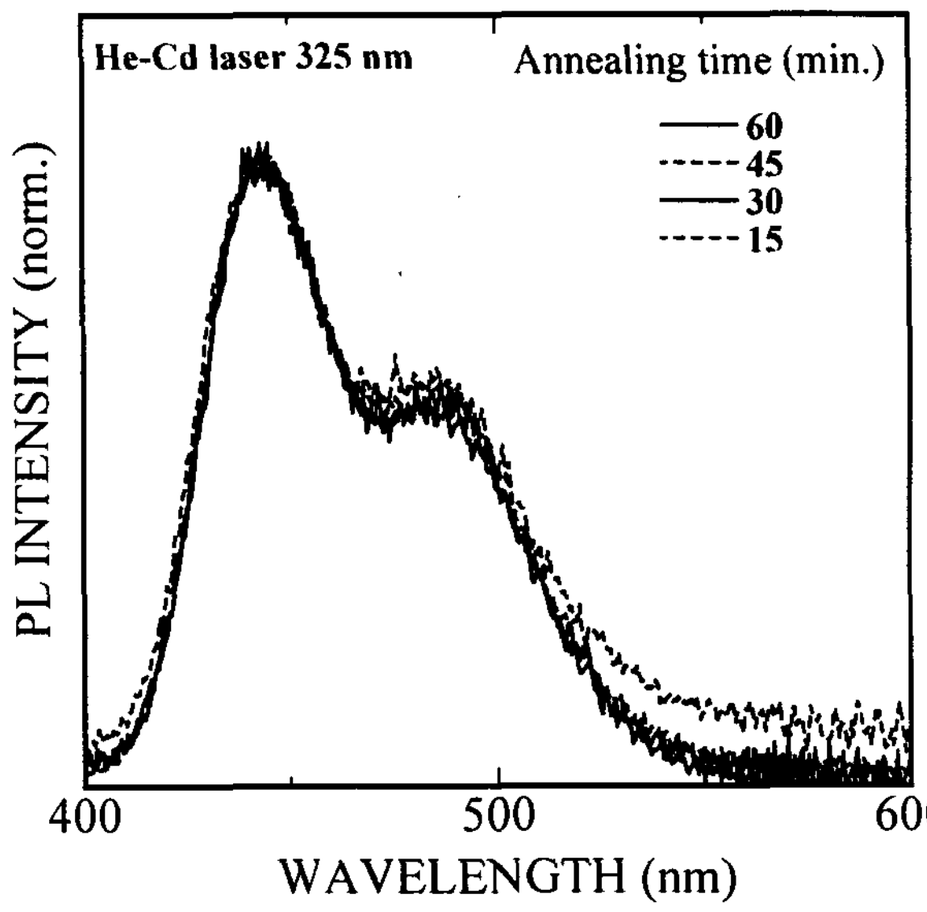

Fig.5 PL spectra of $SrGa_2S_4$:Ce thin films annealed at 800°C for 15, 30, 45 and 60 min in H_2S.

Figure 6 shows CL spectra of the same samples as shown in Fig.5, where the anode voltage (V_a) and current density (J_S) were kept at 2 kV and 60 • A/cm^2, respectively. All of the films show the same blue emission as PL spectra. The CIE color coordinates of the emission shown in Fig.6 are shown in Fig.7. It can be seen that the color

coordinates of the film annealed for 15 to 60 min are very close to that of blue component of CRT. Moreover, the fact that nearly the same spectra were obtained in PL and CL indicates that $SrGa_2S_4$ phase was formed at a whole of the film, because the electron beam only excites the surface of the films while the PL excitation was carried out over the whole film.

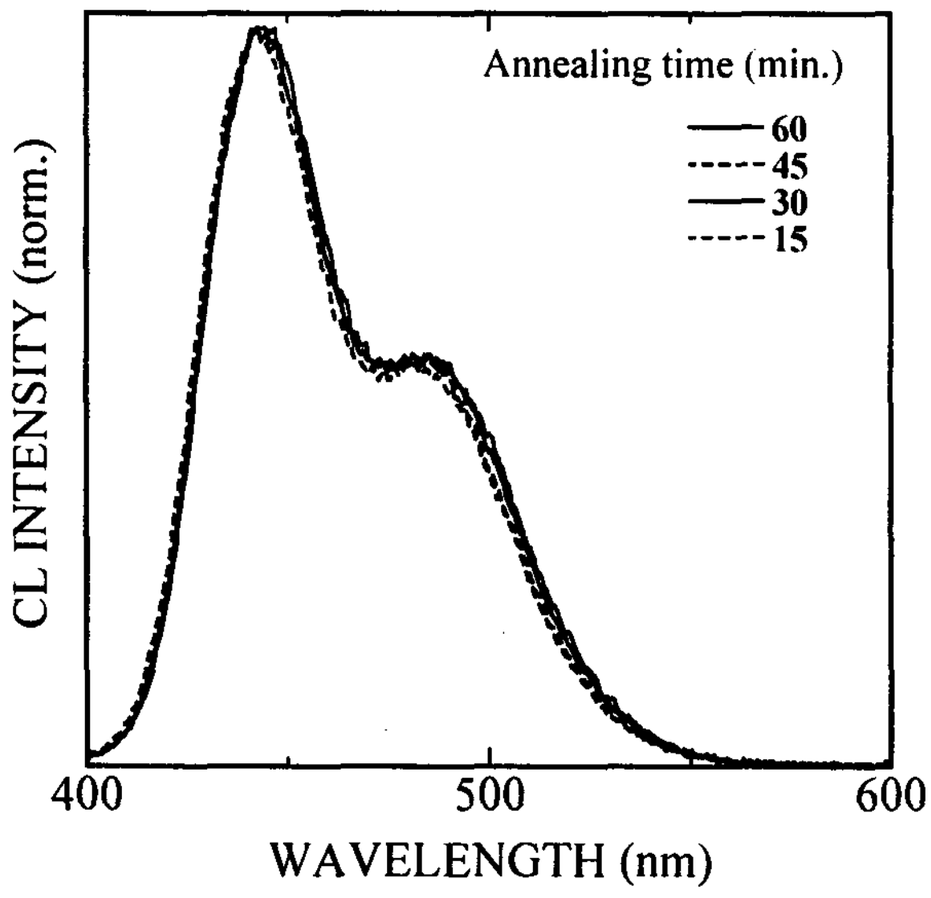

Fig.6 CL spectra of $SrGa_2S_4$:Ce thin films annealed at 800°C for 15, 30, 45 and 60 min in H_2S.

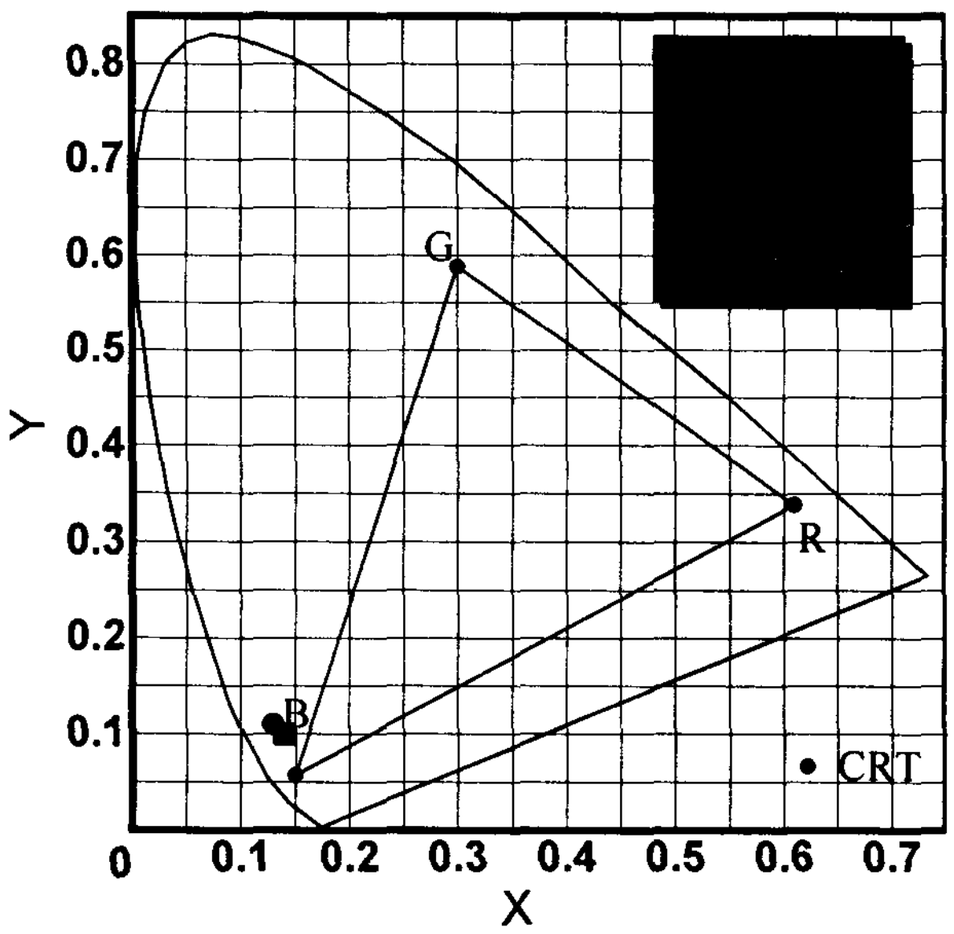

Fig.7 CIE diagram of $SrGa_2S_4$:Ce thin films annealed at 800°C for 15, 30, 45 and 60 min in H_2S.

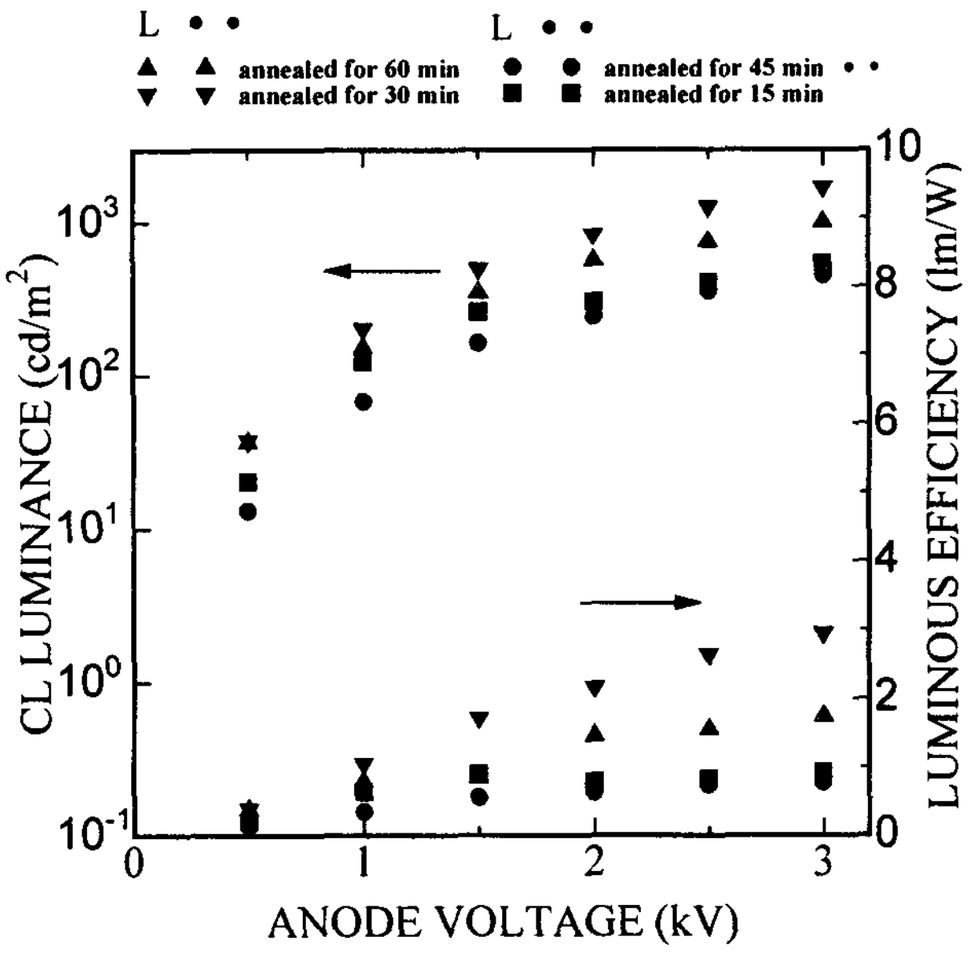

Fig.8 CL luminance and luminous efficiency of $SrGa_2S_4$:Ce thin films deposited at 450°C and annealed at 800°C for 15, 30, 45 and 60 min in H_2S.

Figure 8 shows the CL luminance and luminous efficiency of the $SrGa_2S_4$:Ce thin films, which are same sample as shown in Fig.6, as a function of V_a, where J_S = 60 • A/cm^2. It can be seen that the film annealed at 800•C for 30 min shows highest luminance. The luminance and luminous efficiency of the film annealed for 30 min in H_2S are about 1700 cd/m^2 and 2.95 lm/W, respectively. These data are very high compared with the data reported so far. Whereas, luminance of the films annealed for 45 and 60 min were lower than that of the film annealed for 30 min.

4. Summary

The preparation of $SrGa_2S_4$ thin film phosphors doped with Ce or Eu has been carried out by multi-source deposition technique. It was shown that the as-deposited film was consisted of [001] oriented GaS and probably amorphous Sr phases. The stoichiometric $SrGa_2S_4$ phase is thought to be formed the reaction of these phases and H_2S during

the annealing. Ce-doped films showed blue-emission peaked at 445 and 490 nm due to Ce^{3+} in $SrGa_2S_4$. The $SrGa_2S_4$:Ce thin film annealed at 800•€ for 30 min in H_2S atmosphere showed a luminance of about 1700 cd/m^2 and a luminous efficiency of 2.95 lm/W, respectively under excitation with 3 kV and 60 •A/cm^2. The $SrGa_2S_4$:Eu thin film prepared by same process as the $SrGa_2S_4$:Ce showed green emission peaked at 530 nm due to Eu^{2+} in $SrGa_2S_4$, and 4000 cd/m^2 and 7.05 lm/W. These values are higher than those reported so far for the emission of the thin film phosphors.

5. References

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