Synthesis and luminescence properties of SrS:Eu red phosphors by solid state method

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Abstract

We have synthesized SrS:Eu red phosphor by solid state method and investigated to adopt a red phosphor for LEDs. The SrS:Eu phosphor shows broad emission band at 600nm region due to f-d energy transfer of Eu^{2+}. Our results show that the SrS:Eu red phosphor exhibits the better luminescence efficiency than that of the industrially available product SrS:Eu phosphor.

1. Introduction

LEDs (Light Emitting Diodes) show the high intensity as well as long life time over a million hour. And this becomes the operation to low voltes because electricity energy converts directly to a light energy. Also fast response speed, small size and the light source without the pollution due to taking greatly the attention.

There are two possible structures for a white LEDs. The first is to develop an efficient white-emitting material that can replace the red, green, and blue-emitting materials in LED structure. The other is to embed a single composition, white-emitting material or three-phosphor blend (red, green, and blue-emitting) into the epoxy dome that surrounding the UV-emitting LED.[1,2] Among the three phosphors, we have attempted to develop a red phosphor that emits efficiently under the 405nm~470nm excitation range.

SrS phosphor has been studied extensively long afterglow and thermoluminescence property.[3-5] And this phosphor shows broad emission band and high photoluminescence efficiency at 600nm region. In the present work, we have synthesized SrS:Eu^{2+} red phosphor and investigated the luminescence properties under the 405nm ~ 470nm excitation range. Also SrS:Eu^{2+} red phosphor can be expected to be adopted red phosphors for generation of white light LEDs because of excellency of red region. Therefore, this phosphor can make three-wavelength white LEDs of superior property.

2. Experimental

This study was synthesized SrS:Eu^{2+} by typical solid-state method. Starting materials of SrS:Eu red phosphors were prepared mainly $SrSO_4$ and EuS. Strontium system were experimented SrS (3N, Alfa), $SrSO_4$ (2N, Kanto), $SrCO_3$ (3N, High Purity) and $Sr(NO_3)_3 \cdot xH_2O$ (3N, High Purity) to search most suitable of raw materials. And Europium system were used EuS (3N, High Purity), Eu_2O_3 (4N, High Purity), $Eu(NO_3)_3 \cdot xH_2O$ (3N. High Purity), EuF_3 (3N, High Purity) and $EuCl_3$ (3N, High Purity).

First of all, raw materials are weight, and then mixed by mortar. After, it was dried in the oven at 90℃, 1 hour. This precursor was fired at 900℃~1300℃ in the tube furnace under reduction condition of 5% H_2/ 95% N_2 mixture gas.

The crystallinity of phosphor powder were analyzed by XRD (X-ray Diffractometer : Rikaku DMAX-3) with Cu-Kα radiation. Photoluminescence and excitation spectrum of Phosphor was measured by Perkin Elmer LS-50B spectrometer which was composed of Xenon flash lamp. Emission specta were measured between 500nm and 700nm under excitation wavelength 405 and 465nm. And excitation spectra were scanned from 350nm to 550nm

under an emission wavelength of 600nm. Also phosphor size and shape were observed by SEM (Scanning Electron Microscopy : JEOL JSM6360).

3. Results and discussion

When the SrS:Eu phosphor was prepared using by $SrSO_4$ and EuS, photoluminescence excitation and emission spectra are exhibited Fig. 1. Excitation spectra show high intensity in 420nm~480nm region. And emission peaks have 600nm center wavelength under excitation wavelength of 405nm and 465nm. It is due to f-d energy transfer of Eu^{2+} in host materials. SrS: Eu^{2+} has high intensity in 1050℃. However, this pattern shows not only SrS but also Eu_2O_2S phase.

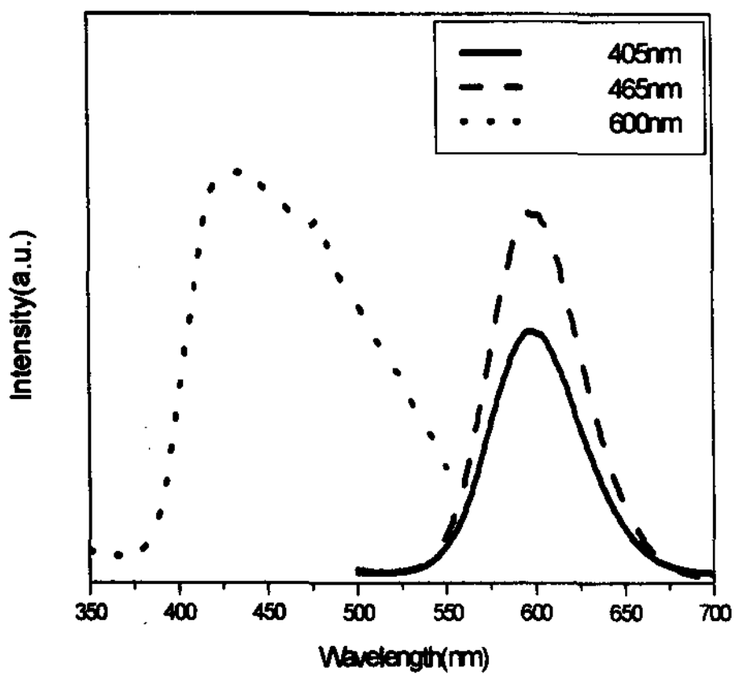

Fig. 1 typical PL excitation and emission spectra of SrS:Eu by solid-state method.

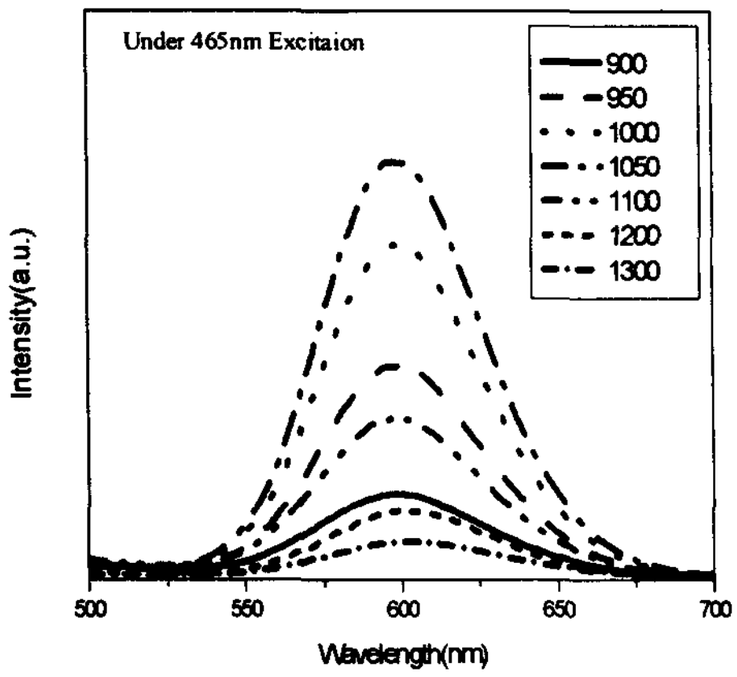

Fig. 2. PL emission spectra of SrS:Eu as change of firing temperature.

We can confirm that we look into the XRD of SrS:Eu heat-treated at different temperature. at 1050℃ peak of Fig. 3, SrS:Eu phosphor have Eu_2O_2S phase. It were supposed to change crystal-field of oxygen from molecular bonding distance or force, dipole-dipole moment, and electron affinity as substitution of sulfide site. But in this work, we could not find out the reason accurately. Just, we realized that it express high efficiency when SrS:Eu phosphor has oxygen phase.

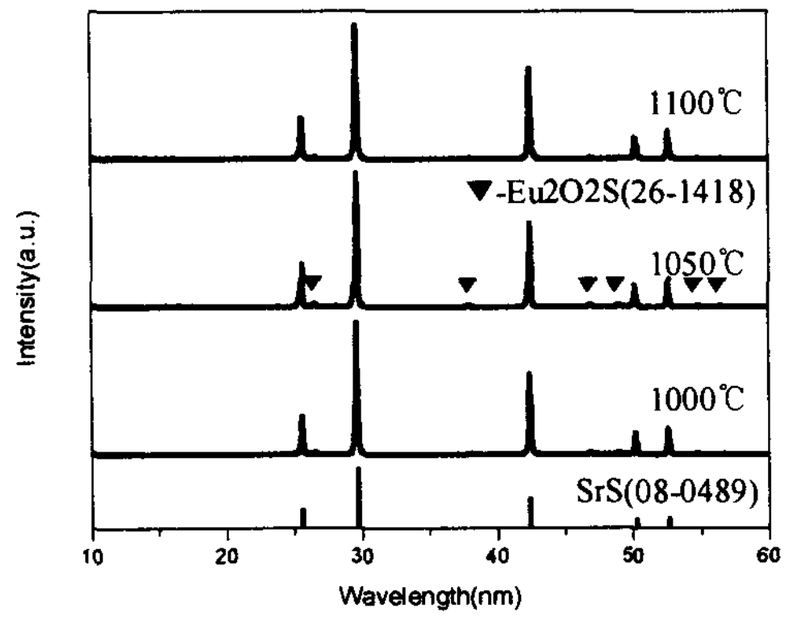

Fig. 3. XRD spectra of SrS:Eu heat-treated at different temperature.

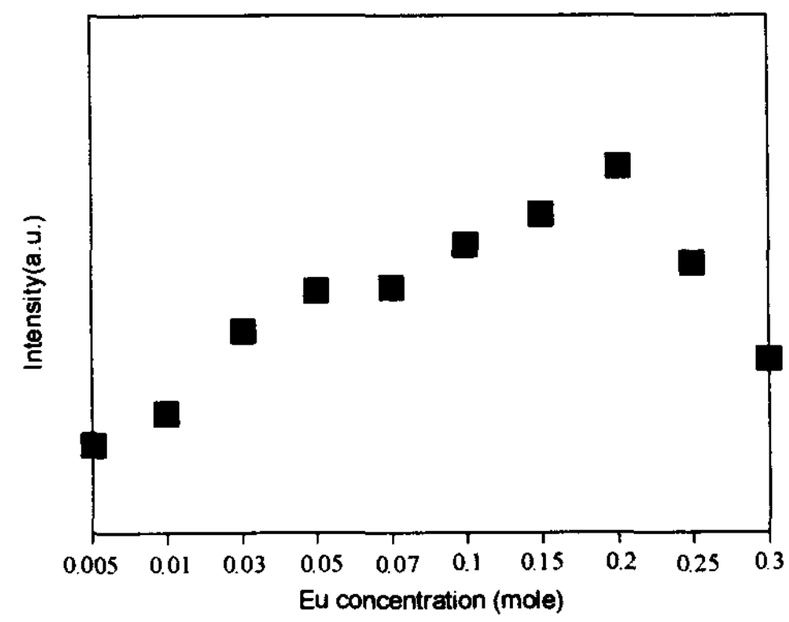

Fig. 4. PL emission intensity of SrS:Eu as a function of Eu concents.

A change of emission intensity is depicted in Fig. 4 at the various Eu^{2+} concentration. The best suitable doping concentration of Eu was evaluated 0.2 mole. The emission intensity was decreased when over doped concentration of 0.2 mole Eu^{2+} ion because of concentration quenching.

That is, emission of Eu^{2+} was absorbed another Eu^{2+} ion. It is because structural of phosphor ununiformity and chemical complexity. Especially, increase of Eu^{2+} ion was cohered or converted killer.[6]

Emission spectra of SrS:Eu are exhibited Fig. 5 and Fig. 6 as change of raw materials. When the SrS:Eu phosphors was synthesized with $SrCO_3$ or $Sr(NO_3)_3 \cdot xH_2O$, these are fired with excess sulfur. Because it is caused of exchange to cation on the heat-treatment. When use of $SrSO_4$ with raw material, it is obtained better highly efficiency than SrS. Accordingly, $SrSO_4$ show most high PL intensity and good luminescence efficiency

Fig. 6 shows emission spectra of SrS:Eu as change of Eu materials. EuS was appeared fine luminescence property, because of unity to the chemical equivalent. Also Europium ion has divalent that they can easily substitution in Sr site as compare with other materials.

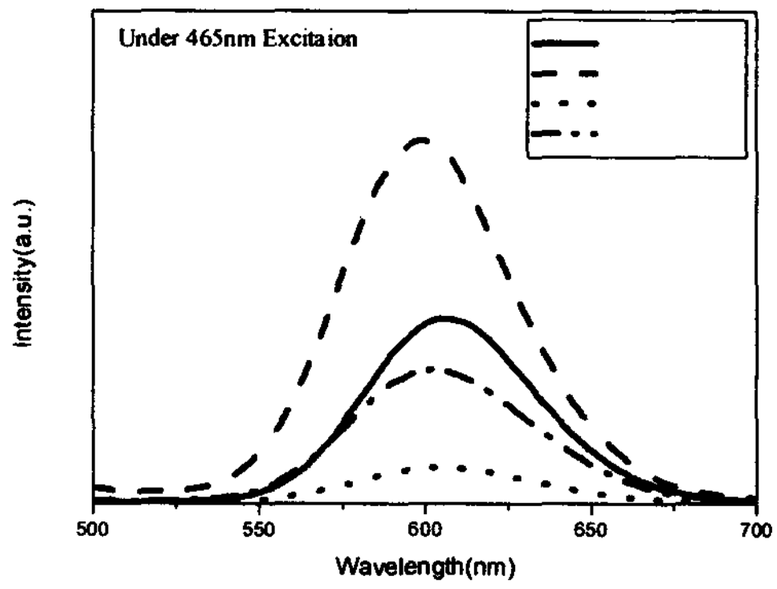

Fig. 5. PL emission spectra of SrS:Eu as change of Sr materials.

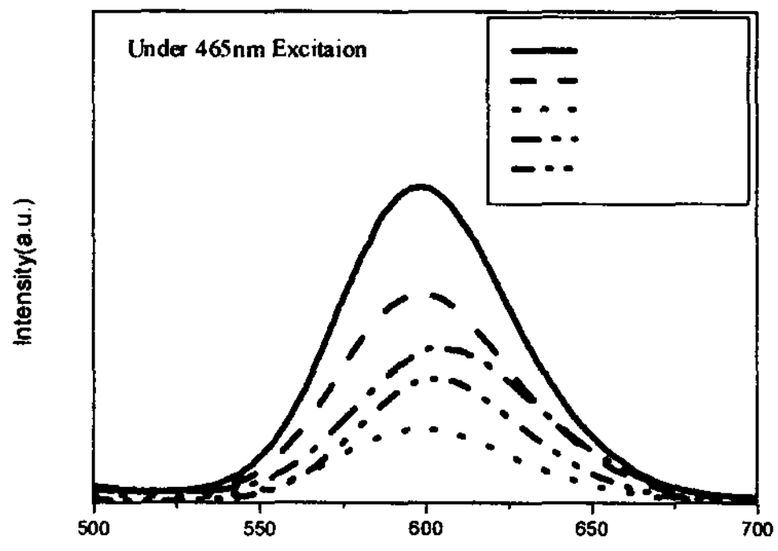

Fig. 6. PL emission spectra of SrS:Eu as change of Eu materials.

Also, particle size and shape of SrS:Eu red phosphors are illustrated Fig. 7. SrS:Eu phorsphors have shap of corneous-circle type. And it have average size of 10㎛. The size must be small to be used for LED(< 20㎛). Therefore, it were fit to application of LED.

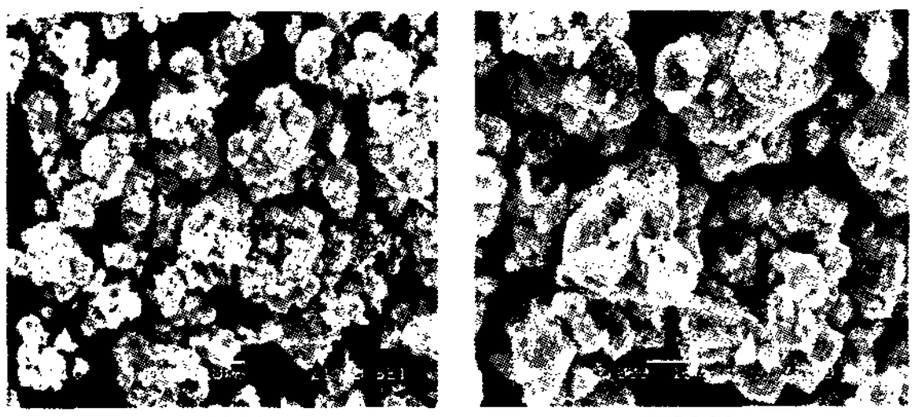

Fig. 7. SEM of SrS:Eu phosphor

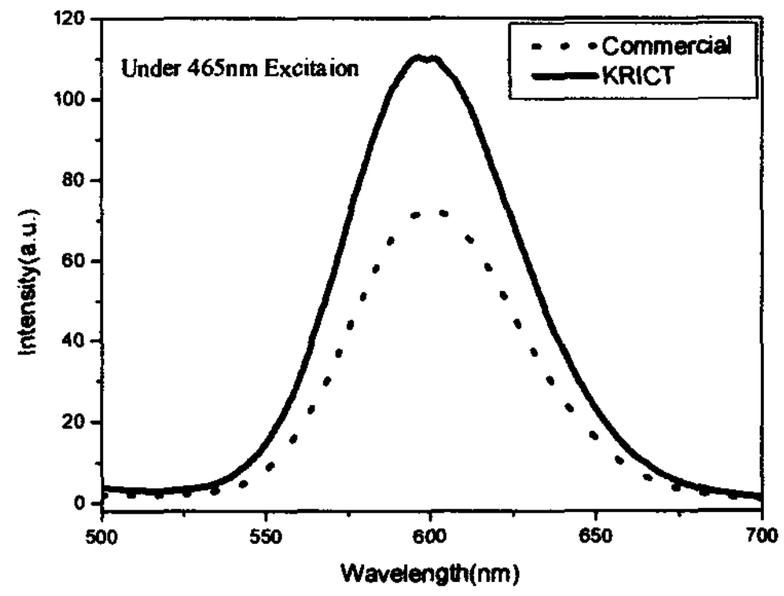

Fig. 8. PL emission spectra of synthesized phosphor compared with commercial SrS:Eu

Lastly, synthesized phosphor(KRICT) compare with commercial red phosphor. It is exhibited Fig. 8. It will be possible to application at a lot of field, also it is that $SrS:Eu^{2+}$ phosphor of red region has immense merit for embody of white LED.

4, Conclusion

In this study, SrS:Eu phosphor was prepared by solid state method using raw materials of sulfide compounds without H_2S gas. When we used the raw materials of SrSO4, EuS, 0.2 mole Eu^{2+} concentration, 100cc/min reduction condition, 1050℃ heat-treated temperature and 3 hours, we obtained the best synthesis condition. SrS:Eu phosphor has various luminescence properties by the

substitution of oxygen element to sulfur site and the coordination of sulfur in the structure. In the near future, it is need to more investigation for application of SrS:Eu phosphor to LEDs.

5. Reference

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