Synthesis of the sulfide phosphors and white light generation based on InGaN chip

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Abstract

$SrGa_2S_4$:Eu green phosphor and SrS:Eu red phosphor have been synthesized by co-precipitation method, respectively. Two sulfide phosphors were influenced by oxygen defect in host materials. Excitation spectra of these phosphors have high efficiency at the long wavelength region. And emission efficiency is increased under the excitation wavelength of 465nm. The combination of thiogallate green phosphor and sulfide red phosphor based on blue light InGaN chip has made it possible to emit white light.

1. Introduction

Nowadays, many researches generating the white light from the LEDs have been studied. White light generation of LEDs can be achieved by combination of three (blue, green and red) diodes or combining a blue LED with green, yellow and/or red emitting phosphor materials which convert part of the incident blue light to their lights.

Some research groups reported that $SrGa_2S_4$:Eu green phosphor convert incident blue light to green light emission. In general, thiogallate phosphors were prepared by conventional preparation method based on the flux method which a mixture of alkaline earth metal carbonate, gallium oxide, rare earth metal oxide and flux agent fired at high temperature (900 ~ 1200 ℃) under the H_2S or CS_2 gas atmosphere. And the conventional synthetic methods of SrS:Eu phosphor are that strontium sulfate and strontium carbonate are reduced with hydrogen sulfide or sulfur at 850 ~ 1050 ℃ and at about 1000 ℃, respectively. However, H_2S is a very toxic gas and can cause serious pollution. Therefore, the exhausted gas must be handled very carefully. For before-mentioned reasons, this research was accomplished by the co-precipitation method and firing technique under H_2/N_2 mixed gas. And then, luminescence properties of two phosphors were compared with those prepared by conventional preparation method. White light LEDs were made by the combination of two phosphors with InGaN chip.

2. Experimental

2.1 Synthesis of $SrGa_2S_4$:Eu phosphor

Eu^{2+} doped $SrGa_2S_4$ green phosphor was prepared by co-precipitation method. Metal sources were $Ga(NO_3)_3 \cdot 5H_2O$ (99.999 %, High Purity Chemicals), $SrCO_3$ (99.9 %, High Purity Chemicals) and Eu_2O_3 (99.99 %, High Purity Chemicals). $(NH_4)_2S$ (Ep, Kanto) was used as a sulfur source, which has been contained 0.5 ~ 1 % sulfur. To prepare appropriate solution, $Ga(NO_3)_3 \cdot 5H_2O$, $SrCO_3$ and Eu_2O_3 were dissolved in the mixed solution of distilled water and acetone (mixed ratio is 1:3). This solution was dropped in 5 ml distilled water and 15 ml acetone. And then, 64ml $(NH_4)_2S$ solution was dropped at the same times. When precipitated, pH was maintained between 9.8 and 10.3 by using nitric acid. After completed dropping, the

precipitate was filtered and dried at 70 ℃. This precursor was fired at 400 ~ 1000 ℃ in the tube furnace under the N_2 (180 cc/min) and H_2 (20 cc/min) mixed gas atmosphere.

2.2 Synthesis of SrS:Eu phosphor

For the synthesis of the europium doped strontium sulfide red phosphor, raw materials were used $SrCO_3$ (99.9 %, High Purity Chemicals), Eu_2O_3 (99.99 %, High Purity Chemicals), Ammonium sulfide (EP, Kanto) and Sulfuric acid (GR, Matsunoen Chemicals LTD.). $SrCO_3$ and Eu_2O_3 were dissolved in distilled water with nitric acid. Ammonium sulfide was dropped in metal ion solution. At the same time, sulfuric acid was added in this solution to maintain pH = 7 ~ 8. The precipitate was filtered and dried at 70℃. This obtained precursor was fired at 950 ℃ in the tube furnace under the mild gas (5 % H_2 and 95 % N_2) atmosphere which could be changed in various flow rate.

2.3 Characterization

The crystallinity of phosphor powder was investigated by X-ray diffractometer (Rikaku DMAX-3) with Cu-Kα radiation and Ni filter. Photoluminescence was measured by Perkin Elmer LS-50B which was composed of Xe-lamp, monochrometer and attenuator. Emission curves were obtained at room temperature by scanning wavelength region from 400 to 750 nm under an excitation wavelength 465 nm. And excitation spectra in powder were measured between 300 and 550 nm under an emission center wavelength.

Luminance properties of white LEDs were investigated by Spectrascan PR650. The combination of various weight ratio of green phosphor to red phosphor with epoxy on the InGaN chip was tested.

3. Results and discussion

3.1 $SrGa_2S_4$:Eu phosphor

The precursors and the sample fired at 500 ℃ had the amorphous phase, the ones fired at 700 ℃ became slowly crystallized to the $SrGa_2S_4$ phase. XRD pattern of the sample of 800 ℃, shows single phase of the $SrGa_2S_4$. However, this XRD pattern exhibits broad pattern between 20 ° and 40 °. It may be attributed to a non-crystalline phase. In the 900 ℃ sample, unusual oxide phase of $SrGa_{12}O_{19}$ except $SrGa_2S_4$ phase was detected. This phase increases at the high temperature of 950 ℃. This tendency could be distinguished on XRD patterns of the sample by the solid-state reaction. Those spectra show only single phase of the $SrGa_2S_4$. Emission spectra of the wet chemical and solid-state method are measured under 465 nm excitation wavelength. As increased firing temperature, the emission intensity is increased until 950 ℃. And then, the luminescent intensity decreased as the firing temperature increased more and more. The emission band of about 519 nm shifts slightly to a longer wavelength of 526 nm according to an increase of firing temperature, as depicted in fig. 1.

Excitation spectra in fig. 2 show large two broad bands, which is separated two regions at the point of 367 nm. The first broad band below 367 nm wavelength is due to the absorption of the host material and transition to split 5d levels of Eu^{2+} ion(?). The second broad band over 367 nm wavelength appeared by the transition of the $4f^7 \rightarrow 4f^6 5d$ levels in the Eu^{2+} ion. 4 In case of solid-state sample and wet chemical synthesized sample fired at 800 ℃, an excitation intensity is slowly decrease from 412 nm to 470 nm, but it is dramatically decreased at above 470 nm. On the other hand, the slope of the excitation spectrum in the range of 412 nm ~ 470 nm, in case of wet chemical

prepared sample fired at 1000 ℃, is nearly linear. And the dramatic decreasing point of 470 nm is shifted to 478 nm.

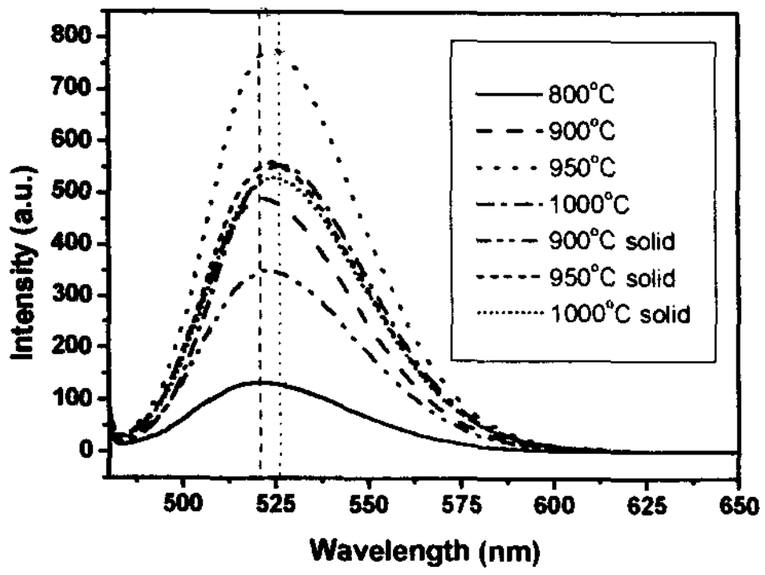

Fig. 1 PL emission spectra of $SrGa_2S_4$:Eu under the excitation wavelength of 465nm.

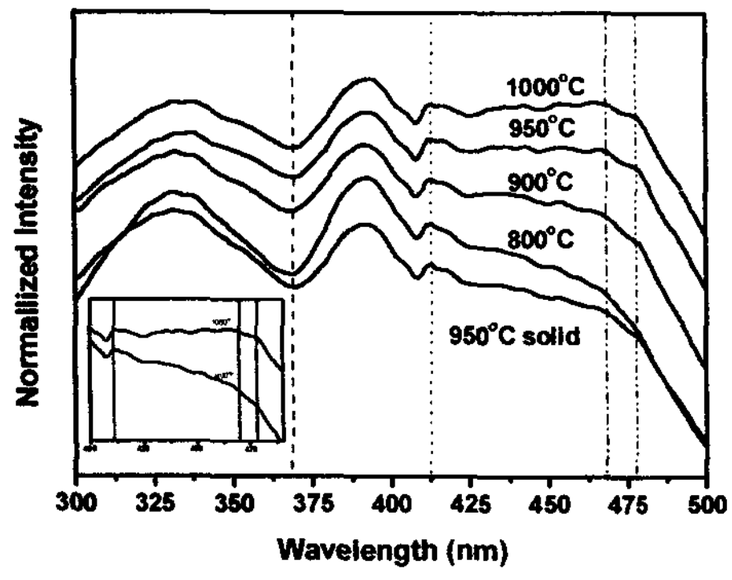

Fig. 2 Excitation spectra of $SrGa_2S_4$:Eu

3.2 SrS:Eu phosphor

Emission and excitation spectra are exhibited fig. 3 and fig. 4, respectively. The oxygen contents of samples prepared by the various gas flow rate are analyzed by elementary analysis. Oxygen contents are changed from 0.27 % to 5.3 %. The emission intensities are changed by the gas flow rate. As gas flow rate increases, the emission intensity reduces. The main emission peak center shifts to blue region, that is, from 606 nm at the 300cc gas flow to 600 nm at the 50 cc gas flow. It can be supposed that excitation spectra affect by the oxygen defect. As gas flow rate decreases, the excitation intensity increases. The excitation intensity increases upto 418 nm in the case of 300 cc gas flow. However, at the 50 cc gas flow, the excitation intensity increases continuously up to 425 nm, decreased slowly from 425 nm and decreases rapidly over 482 nm region.

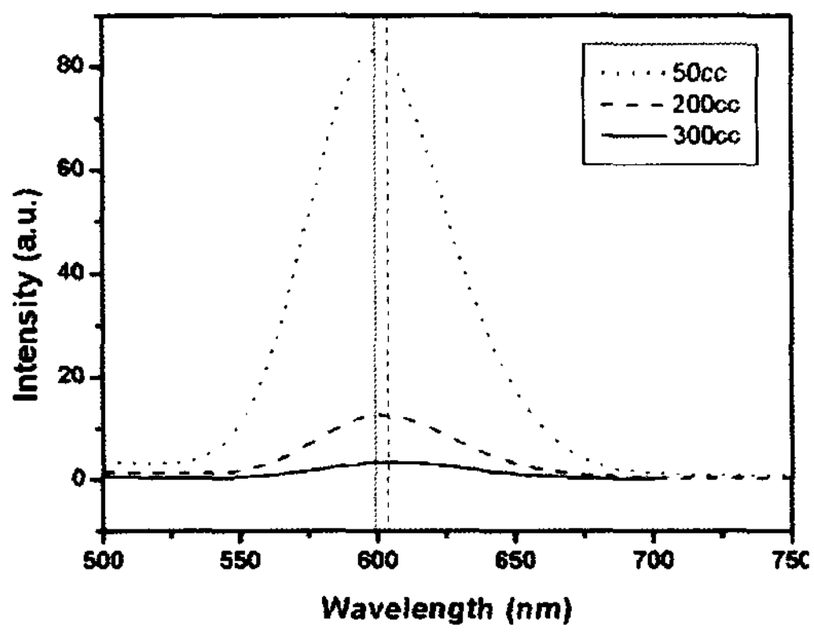

Fig. 3 Emission spectra of SrS:Eu phosphor at the various gas flow rates

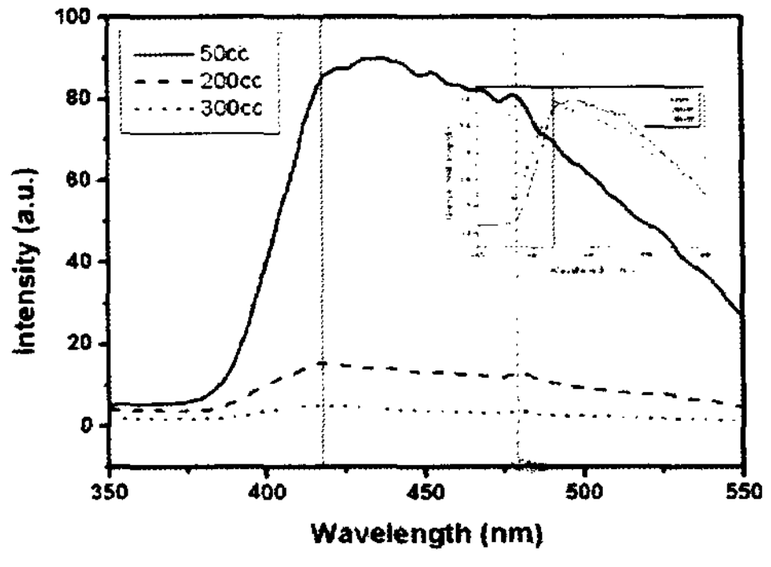

Fig. 4 Excitation spectra SrS:Eu at the various gas flow rates

3.3 White Light LED

The combination of thiogallate green phosphor and

sulfide red phosphor with blue light InGaN chip could be applicable to emit white light in LEDs. Different weight ratios of two phosphors on InGaN chip result in from white to gold light in LED.

4. Conclusion

In this study, europium doped strontium thiogallate and strontium sulfide phosphor have been prepared by the co-precipitation method and treated successively at several heating conditions under the mild hydrogen gas atmosphere without H_2S gas. These two phosphors have high green and red emission peak under the excitation wavelength of 465 nm, respectively. These phosphors have high efficiency at long wavelength region. The combination of thiogallate green phosphor and sulfide red phosphor based with blue light InGaN chip can generate white light in LEDs.

5. References

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