Photoluminescence Properties of SrGa$_2$S$_4$:xCe Blue-Emitting Phosphor

A. R. Gharpure$^1$, Dr. S. P. Wankhede$^2$

$^1$Department of Physics, R.T.M.N.U., Nagpur, Maharashtra, India

$^2$Associate Professor, Department of Physics, K. D. K. College of Engineering, Nagpur, Maharashtra, India

Abstract: The synthesis method and photoluminescence properties of Ce$^{3+}$ doped SrGa$_2$S$_4$ phosphors for white light emitting diode (LEDs) are reported. The excitation spectrum of synthesized phosphors consists of band between 250 nm and 430 nm respectively. SrGa$_2$S$_4$:Ce$^{3+}$ shows the blue emission band at about 445 nm due to Ce$^{3+}$ transition from 5d state to 4f state for 410 nm excitation. The effect of different dopant concentration on the PL emission was also investigated. Maximum PL intensity was observed when SrGa$_2$S$_4$ was doped with 1.5 mole % of Ce$^{3+}$. SrGa$_2$S$_4$:Ce$^{3+}$ is used as blue emitting phosphor excited by a near-UV LED.

Keywords: Photoluminescence, SrGa$_2$S$_4$:Ce$^{3+}$ phosphors, near-UV LED

1. Introduction

The alkaline earth thiogallate are the basis of new type of sulphide phosphor. Rare ions readily substitute for the alkaline earth in the host lattice resulting in phosphors that fluorescence strongly under UV and cathode rays[1]. The efficient sulphide phosphors based on rare earth activator were those described by Urbach [2], Ward [3] and their associates beginning in 1946-1947. These are the infrared stimulable alkaline earth sulphides doubly activated with Ce$^{3+}$, Eu$^{2+}$ and Eu$^{3+}$. Keller and co-workers [4] later reported on the fluorescence of virtually all of the rare earth ions in SrS and recently Lehmann and Ryan [5] presented data on the cathodoluminescence of CaS, Ce$^{3+}$ and SrS: Eu$^{2+}$. Although, the alkaline earth sulphides are efficient host for rare earth ions, phosphors of this type have not been widely used because of their susceptibility to hydrolysis. It was decided therefore, to investigate binary compound based on the alkaline earth sulphide. Since these materials should readily accommodate substitutional rare earth ions and might also be more stable towards hydrolysis [1].

It has been shown [6] that the band gap of a binary chalcogenide compound can be estimated from the arithmetic mean of the band gap of the unary components. The absorption spectra of SrS have been determined [7] and consequently the band gap is known to be about 4.05 eV. Initially, the activators chosen for the study included those in which 4f$^{1}$ 5d → 4f$^{1}$ transitions were known to play an important role in the emission process (i.e. Ce$^{3+}$, Eu$^{2+}$, Yb$^{3+}$). Of these only Ce$^{3+}$ and Eu$^{2+}$ were found to exhibit visible emission. Recent studies have demonstrated that SrGa$_2$S$_4$:Ce$^{3+}$ phosphor is well excited by photons which are absorbed by the host-crystal atoms, and energy transfer probably occurs between the thiogallate lattice and Ce$^{3+}$ ions, leading ultimately to some radiative recombination within the localized activator states [8, 9]. Peters and Baglio [1] in 1972 thoroughly investigated photoluminescence of thiogallate phosphors activated with Ce$^{3+}$ and Eu$^{2+}$. The MGa$_2$S$_4$ type thiogallates are suitable host materials for absorption of near-UV and visible light because they have band gaps below 4.0 eV [1]. These materials are more stable towards hydrolysis. Among these, SrGa$_2$S$_4$ and ZnGa$_2$S$_4$ were later developed into commercial phosphors. SrGa$_2$S$_4$ is a versatile luminescent material. All three primary colours can be generated using various activators or some combinations thereof [1]. SrGa$_2$S$_4$:Eu$^{2+}$ is suitable green emitting phosphor excited by blue and near UV LED and SrGa$_2$S$_4$:Ce$^{3+}$ is used for blue emitting phosphor excited by near-UV LED [10].

Thiogallate compound represented by the formula MGa$_2$S$_4$ (where M=Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Pb$^{2+}$, Eu$^{2+}$) were prepared by dissolving sulphur in an aqueous solution of hydrazine hydrate. The solution was combined with solution of an appropriate two or more cations to produce ternary compounds of sulphur for example thiogallates. The method is particularly applicable to the production of doped phosphor by the inclusion of solutions containing the appropriate dopent. An important feature of the method described herein is the dissolution of elemental sulphur, which can be of a high priority, by chemical reaction with hydrazine. This may be expressed as:

$$N_2H_4+2X=N_2+2H_2X$$

(where X=S)

The hydrazine is preferably in the form of hydrazine hydrate. In this paper we synthesized SrGa$_2$S$_4$:xCe$^{3+}$ phosphor by wet chemical co-precipitation method using solution of sulphur in hydrazine hydrate. The photoluminescence, structural properties, and cerium concentration of PL emission spectra of SrGa$_2$S$_4$:Ce$^{3+}$ were investigated.

2. Experimental

The wet chemical co-precipitation method was used to prepare the ternary sulphide SrGa$_2$S$_4$: Ce$^{3+}$ phosphor with varying concentration of Ce$^{3+}$. Strontium chloride(99.9% A. R. Grade), Gallium acetate and sulphur were used as the activator. Gallium acetate was prepared by dissolving Gallium oxide (99.9%, A. R. Grade) in acetic acid and evaporating the excess acid. The sulphur was dissolved in an aqueous solution of hydrazine hydrate (solution 1).

The synthesis method and photoluminescence properties of Ce$^{3+}$ doped SrGa$_2$S$_4$ phosphors for white light emitting diode (LEDs) are reported. The excitation spectrum of synthesized phosphors consists of band between 250 nm and 430 nm respectively. SrGa$_2$S$_4$:Ce$^{3+}$ shows the blue emission band at about 445 nm due to Ce$^{3+}$ transition from 5d state to 4f state for 410 nm excitation. The effect of different dopant concentration on the PL emission was also investigated. Maximum PL intensity was observed when SrGa$_2$S$_4$ was doped with 1.5 mole % of Ce$^{3+}$. SrGa$_2$S$_4$:Ce$^{3+}$ is used as blue emitting phosphor excited by a near-UV LED.
excess of hydrazine hydrate was used with at least 2:1 mole ratio of hydrazine hydrate to the sulphur. The stoichiometric amount of Gallium acetate was dissolved in water in one beaker. The stoichiometric amount of Strontium chloride was dissolved in water in another beaker. These aqueous solutions were mixed with (solution 1) with stirring. The mixture was stirred for 30 min and then filtered. The ppt so obtained was washed with one litre of water and dried at 110°C. Appropriate amount of Europium acetate was slurried in with the help of 2-propanol. The mixture was transferred to silica crucible and reduced at 900 ºC for one hour. X-ray diffraction pattern was recorded on Philips PAN analytical expert pro-diffractometer. PL characteristics in the range 200 nm – 700 nm at room temperature were studied using Hitachi F-7000 spectrophotometer, with 1.5 nm spectral slit width.

3. Results and Discussion

SrGa₂S₄: xCe³⁺ phosphors were prepared by wet chemical co-precipitation. Fig.1 shows XRD pattern of SrGa₂S₄: xCe³⁺ phosphors. It is seen that pattern matches excellently with ICDD file no. 25-0895. The crystal structure of SrGa₂S₄ is orthorhombic with a = 20.840 Å, b = 20.495 Å, c = 12.212Å.

**Figure 1: XRD of SrGa₂S₄:Ce³⁺**

Excitation and Emission Spectra of Ce³⁺ activated SrGa₂S₄ Phosphor

Fig.2 shows photoluminescence excitation and emission spectrum of SrGa₂S₄:xCe³⁺ (for x=1 mole %). Excitation spectrum monitored at 445 nm emission exhibit broad excitation band ranging from 250-430 nm. Host SrGa₂S₄ has a moderately large band gap of about 4.4 eV. The principle excitation band must be due to Ce³⁺ absorption. The shorter wavelength excitation bands are due to host absorption. These bands may be attributed to electronic transition from 4f ground state to crystal field split 5d state of Ce³⁺ ions [10].

**Figure 2: PL excitation and emission spectra of SrGa₂S₄:xCe³⁺ (for x=1 mole %) A) Excitation spectra for 445 nm emission, B) Emission spectra for 280 nm excitation, C) Emission spectra for 254 nm excitation**

Photoluminescence measurements showed that the phosphor exhibited typical Ce³⁺ emission. The emission spectrum is peaking at 445 nm corresponding to 5d→4f electronic transition of Ce³⁺. Although visible emission has been reported, the fluorescence is usually characterized by broad bands appearing in the near ultraviolet region of the spectrum [1].

Fig.3 represents the emission spectra of SrGa₂S₄:xCe³⁺ doped with different concentration of Ce³⁺ for the excitation at 280 nm. The emission intensity of Ce³⁺ doped thiogallate as a function of activator concentration was investigated in a series of sample prepared with cerium contents ranging from 0.1 to 3 mol %. Maximum intensity was observed for Ce³⁺ concentration of 1.5 mole %.

**Figure 3: Photoluminescence spectra of SrGa₂S₄:xCe³⁺ phosphors at different values x for λex=280 nm.**

Fig.4 shows the curve of the normalized emission intensity vs activator Ce³⁺ concentration for SrGa₂S₄:xCe³⁺ phosphor. Curve shows increase in intensity with increasing cerium substitution and above 1.5 mol % Ce³⁺, intensity decreases. It shows a concentration quenching of the phosphors.

**Figure 4: Curve of the normalized emission intensity vs activator Ce³⁺ concentration for SrGa₂S₄:xCe³⁺ phosphor.**
4. Conclusion

A blue emitting phosphor SrGa$_2$S$_4$:Ce$^{3+}$ was synthesized by wet chemical co-precipitation method. SrGa$_2$S$_4$:Ce$^{3+}$ are isomorphous and belong to orthorhombic space group D$_{2h}^{24}$ – Fddd. Dependence of PL emission intensity on Cerium concentration was determined. The optimum Ce$^{3+}$ concentration for PL emission intensity was found to be 1.5 mole %. SrGa$_2$S$_4$:Ce$^{3+}$ has excellent photoluminescence properties and can be promising blue emitting phosphor for applications of white LED excited by near-UV.

References


