

Photoluminescence Properties of SrGa₂S₄:xCe Blue-Emitting Phosphor

A. R. Gharpure¹, Dr. S. P. Wankhede²

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

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

Abstract: The synthesis method and photoluminescence properties of Ce³⁺ doped SrGa₂S₄ 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. SrGa₂S₄:Ce³⁺ shows the blue emission band at about 445 nm due to Ce³⁺ 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 SrGa₂S₄ was doped with 1.5 mole % of Ce³⁺. SrGa₂S₄:Ce³⁺ is used as blue emitting phosphor excited by a near-UV LED.

Keywords: Photoluminescence, SrGa₂S₄:Ce³⁺ phosphors, near-UV LED

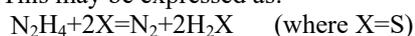
1. Introduction

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 fluoresce 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 stimulative alkaline earth sulphides doubly activated with Ce³⁺, Eu²⁺ and Eu²⁺, Sm³⁺. 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:Ce³⁺ and SrS:Eu²⁺. 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 4fⁿ⁻¹ 5d → 4fⁿ transitions were known to play an important role in the emission process (i.e. Ce³⁺, Eu²⁺, Yb²⁺). Of these only Ce³⁺ and Eu²⁺ were found to exhibit visible emission. Recent studies have demonstrated that SrGa₂S₄:Ce³⁺ phosphor is well excited by photons which are absorbed by the host-crystal atoms, and energy transfer probably occurs between the thiogallate lattice and Ce³⁺ 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 Ce³⁺ and Eu²⁺. The MGa₂S₄ 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, SrGa₂S₄ and ZnGa₂S₄ were later developed into commercial phosphors. SrGa₂S₄ is a versatile luminescent material. All three primary colours can be generated using various activators or some combinations thereof [1]. SrGa₂S₄:Eu²⁺ is suitable green emitting phosphor excited by blue and near UV LED and SrGa₂S₄:Ce³⁺ is used for blue emitting phosphor excited by near-UV LED [10].

Thiogallate compound represented by the formula MGa₂S₄ (where M=Ca²⁺, Sr²⁺, Ba²⁺, Pb²⁺, Eu²⁺) 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:



The hydrazine is preferably in the form of hydrazine hydrate. In this paper we synthesized SrGa₂S₄:xCe³⁺ 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 SrGa₂S₄:Ce³⁺ were investigated.

2. Experimental

The wet chemical co-precipitation method was used to prepare the ternary sulphide SrGa₂S₄:Ce³⁺ phosphor with varying concentration of Ce³⁺. 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). An

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 slurred in with the help of 2-propanol. The mixture was transferred to silica crucible and reduced at 900 °C 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

$\text{SrGa}_2\text{S}_4: x\text{Ce}^{3+}$ phosphors were prepared by wet chemical co-precipitation. Fig.1 shows XRD pattern of $\text{SrGa}_2\text{S}_4: x\text{Ce}^{3+}$ phosphors. It is seen that pattern matches excellently with ICDD file no. 25-0895. The crystal structure of SrGa_2S_4 is orthorhombic with $a = 20.840 \text{ \AA}$, $b = 20.495 \text{ \AA}$, $c = 12.212 \text{ \AA}$.

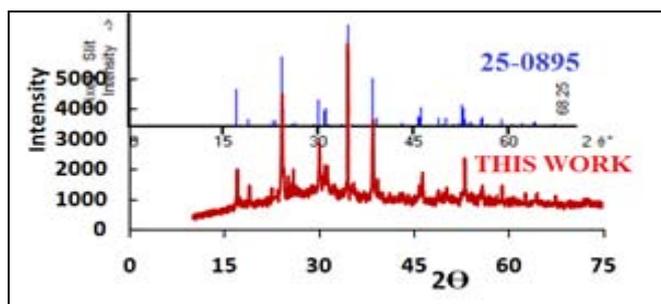


Figure 1: XRD of $\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$

Excitation and Emission Spectra of Ce^{3+} activated SrGa_2S_4 Phosphor

Fig.2 shows photoluminescence excitation and emission spectrum of $\text{SrGa}_2\text{S}_4:x\text{Ce}^{3+}$ (for $x=1$ mole %). Excitation spectrum monitored at 445 nm emission exhibit broad excitation band ranging from 250-430 nm. Host SrGa_2S_4 has a moderately large band gap of about 4.4 eV. The principle excitation band must be due to Ce^{3+} absorption. The shorter wavelength excitation bands are due to host absorption. These bands may be attributed to electronic transition from $4f^1$ ground state to crystal field split $5d^1$ state of Ce^{3+} ions [10].

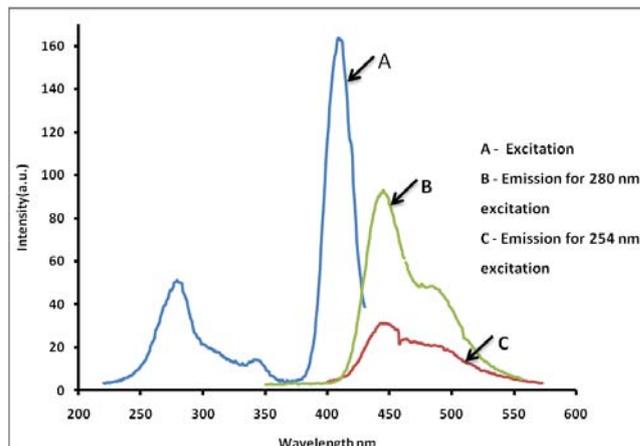


Figure 2: PL excitation and emission spectra of $\text{SrGa}_2\text{S}_4:x\text{Ce}^{3+}$ (for $x=1$ mole %) A) Excitation spectra for 445 nm emission, B) Emission spectra for 280 nm excitation, C) Emission spectra for 254 nm excitation

Photoluminescence measurements showed that the phosphor exhibited typical Ce^{3+} emission. The emission spectrum is peaking at 445 nm corresponding to $5d \rightarrow 4f$ electronic transition of Ce^{3+} . 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 $\text{SrGa}_2\text{S}_4:x\text{Ce}^{3+}$ doped with different concentration of Ce^{3+} for the excitation at 280 nm. The emission intensity of Ce^{3+} 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 mole %. Maximum intensity was observed for Ce^{3+} concentration of 1.5 mole %.

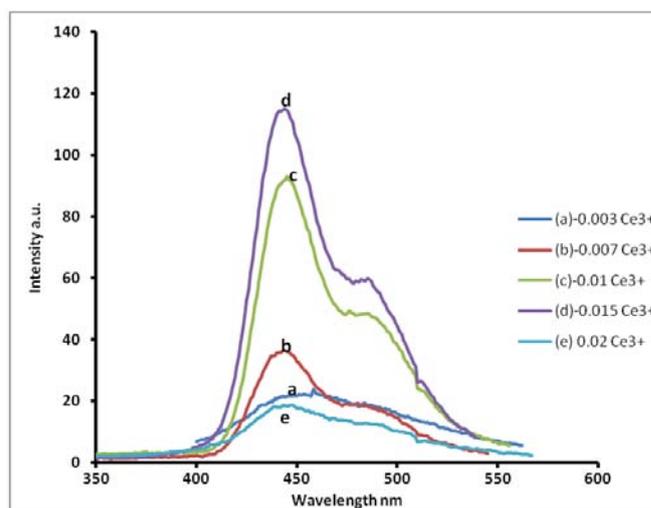


Figure 3: Photoluminescence spectra of $\text{SrGa}_2\text{S}_4:x\text{Ce}^{3+}$ phosphors at different values x for $\lambda_{\text{ex}}=280 \text{ nm}$.

Fig.4 shows the curve of the normalized emission intensity vs activator Ce^{3+} concentration for $\text{SrGa}_2\text{S}_4:x\text{Ce}^{3+}$ phosphor. Curve shows increase in intensity with increasing cerium substitution and above 1.5 mol % Ce^{3+} , intensity decreases. It shows a concentration quenching of the phosphors.

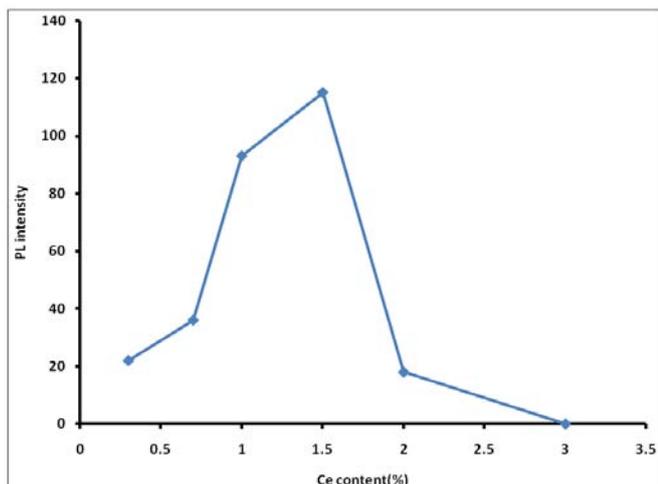


Figure 4: Ce^{3+} concentration dependence of PL intensity. Fig.5 shows CIE colour coordinates of the phosphors $\text{SrGa}_4\text{S}_4:\text{xCe}^{3+}$. The colour coordinates CIE 1931 for the as-synthesized phosphors are ($x=0.1406$, $y=0.0973$). The CIE chromaticity coordinates of blue NTSC (National Television Standard Committee) are $x = 0.14$, $y = 0.08$. The CIE chromaticity coordinate of SrGa_4S_4 are close to those of blue NTSC. Therefore, SrGa_4S_4 have blue-emitting colour purities.

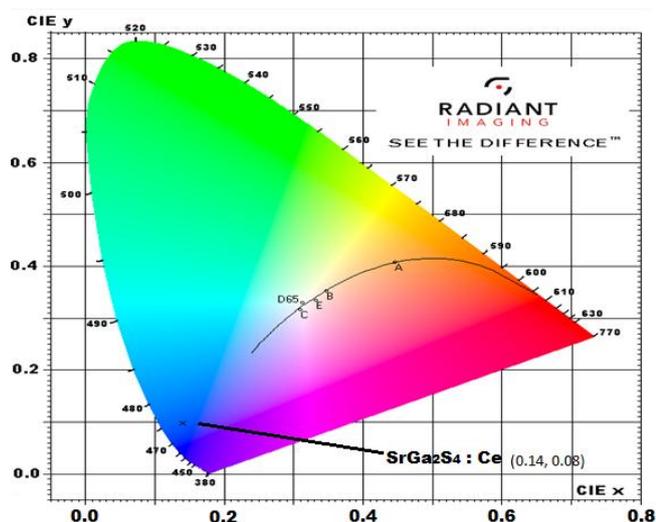


Figure 5: CIE colour coordinates of SrGa_4S_4

4. Conclusion

A blue emitting phosphor $\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$ was synthesized by wet chemical co-precipitation method. $\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$ are isomorphous and belong to orthorhombic space group $D_{2n}^{24} - Fddd$. 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 %. $\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$ has excellent photoluminescence properties and can be promising blue emitting phosphor for applications of white LED excited by near-UV.

References

[1] T. E. Peters and J. A. Baglio, "Luminescence and structural property of Thiogallate phosphors Ce^{3+} and Eu^{2+} - Activated phosphors" Part-1, Journal of

Electrochemn. Soc.; Solid State Sci. and Techno., 119-230 (1972)

[2] Franz Urbach, Donald Pearlman, and Henry Hemmendinger. "On Infra-Red Sensitive Phosphors 1-3": J. Opt. Soc. Am. 36(7), 372-381 (1946)

[3] E. Banks, V. J. Russo, R. Ward. "The Preparation of Pure Magnesium Sulfide and its Use as a Base Material for Infrared Phosphors"; J.A m. Chem. Soc. 72, 3173-3176 (1950) DOI: 10.1021/ja01163a101

[4] Seymour P. Keller; "Fluorescence Spectra, Term Assignments, and Crystal Field Splittings of Rare Earth Activated Phosphors"; J. Chem. Phys. 29, 180 (1958)

[5] W. Lehman and F. M. Ryan, "Cathodoluminescence of $\text{CaS} : \text{Ce}^{3+}$ and $\text{CaS} : \text{Eu}^{2+}$ phosphors", Journal of Electrochemn. Soc.; Solid State Sci. and Techno., Vol. 118, 0477 (1971)

[6] Zinc-indium-sulfide : a new photoconductor R. Nitsche and W. J. Merz, Helv. Phys. Acta, 35, 274 (1962)

[7] Studies on Some Infrared Stimulable Phosphors S. P. Keller, J. E. Mapes and G. Cheroff, Phys. Rev, 108, 663 (1957)

[8] S-S. Sun and R. T. Tuenge, J. Kane and M. Ling, "Electroluminescence and Photoluminescence of Cerium-Activated alkaline earth Thiogallate thin film and devices," Journal of Electrochemn. Soc., Vol. 141 No. 10, 2877 (1994)

[9] O. N. Djazovski, T. K. Mikami, K. Dhmi, STanak, H. Kobayashi, "Luminescence and energy transfer in thin films of $\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$ ", Journal of Electrochem. Soc. 146, 1215-1221 (1999)

[10] C. Chartier, C. Barthou, P. Belalloul, J. M. Frigerio "Photoluminescence of Eu^{2+} in SrGa_2S_4 ", "Journal of Luminescence", Vol. 111, 147-158 (2005)