Digest Journal of Nanomaterials and Biostructures Vol. 5, No 4, October-December 2010, p. 829-835

ELECTROLUMINESCENCE STUDY OF ZnS: Sm, Li PHOSPHOR USING SOLID STATE REACTION METHOD

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In the present work we have attempted to study the electroluminescent (EL) properties of ZnS: Sm, Li luminophor.The phosphor is synthesized using solid state reaction method. A comparative study has been made for electroluminescent emission characteristics of five samples viz ZnS:Cu,Li, ZnS:Sm, ZnS:Sm,Cl; ZnS:Sm,Li; ZnS:Cu,Sm,Li. It is observed that the intensity of brightness varies with the applied voltage and excitation frequency according to the universal laws and color of emission is found to be greenish. Li is found to enhance the EL intensity of ZnS: Sm phosphor. Structural studies using XRD have also been performed. The average grain size of ZnS: Sm, Li is estimated to be 38.9µm

(Received July 27, 2010; accepted October 14, 2010)

Keywords: Electroluminescence, Excitation frequency, Luminophor, XRD

1. Introduction

Electroluminescence (EL) is a phenomenon that converts electrical energy to luminous energy without thermal energy generation. Zinc sulphide is one of the most investigated materials for electroluminescence. It has been observed that thin film, single crystals, semiconductors and impurity doped ZnS exhibit EL phenomenon. [1, 2, 3]. Cu is well studied conventional activator and presence of Cu_2S phase is considered essential for EL excitation [4, 5, 6]. ZnS: Cu with co-activator Cl is also well studied. [7, 8, 9]. There are also reports on ZnS: Cu with co- activators other than Cl [10, 11, 12]. Attempts have also been made to study the behavior of manganese ions and silver ions apart from Cu in ZnS lattice [13, 14]. Electroluminescence of rare earth ions doped ZnS phosphors has got attention due to transitions between energy states of the partially filled and well shielded 4f shells. Maheshwari et al. [15] have reported the effect of Sm and Cu, Sm doping in ZnS lattice. Similarly Srivastava et al. [16] have studied Sm doping in ZnS. Kobayashi et. al [17] have studied the luminescent characteristics of CaS: Sm with six group of lines.Tzu et al. [18] have reported photoluminescent properties of ZnS: Sm without any Cu doping.

In this report we have chosen Sm as the activator. We have tried to enhance EL characteristics of ZnS: Sm by adding Li as the co-activator. The effect of Li doping is studied by comparative study of ZnS:Sm(0.5%,); ZnS:Cu,Li(0.1%,1.0%); ZnS:Sm,Cl(0.5%,1.0%); ZnS:Sm,Li(0.5%,1.0%); and ZnS:Cu,Sm,Li(0.1%,0.5%,1.0%) samples prepared under similar conditions.

2. Experimental section

2.1 Sample preparation

For the preparation of samples pure (luminescent grade) zinc sulphide is taken as the starting material. Soluble salt solutions of samarium oxide, lithium acetate and cupric sulphate

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(AR grade) were added to ZnS containing proper percentage of activator(s) and co-activator(s). The mixture was then thoroughly pulverized and slowly dried up at about 80^0C. The mixture was then powdered and put in carbon capped quartz tube to avoid oxidation. It was then fired at a temperature of 800^0 C for 30 minutes in a cylindrical furnace in controlled condition. Five different phosphor samples viz ZnS:Sm(0.5%,);ZnS:Sm,Cl(0.5%,1.0%);ZnS:Sm,Li(0.5%,1.0%); and ZnS:Cu, Sm, Li (0.1%,0.5%,1.0%) were prepared employing this technique.

2.2 Instrumentation

For measurement purpose the sandwich type EL cells have been used. The cells were prepared by sandwiching the phosphor material suspended in polystyrene binder between two parallel plates. The lower plate was of plane polished Al sheet and the upper one was transparent conducting glass sheet. For casual testing and measurements, temporary cells were used with castor oil medium. The cell was excited with oscillator cum amplifier assembly in 0-50 KHz range and the output was recorded with IP 21PMT. For spectral analysis interference filters were used of wavelengths ranging from 4066 A^0-6912 A^0.The crystal structure of ZnS and ZnS:Sm,Li luminophors were characterized by X-ray diffraction (XRD) using Rigaku D/MAX- 2200H/PC, Cu Kα radiation.

3. Results and discussion

3.1 Structural study

Fig. 1 shows the XRD pattern for ZnS: Sm, Li phosphors synthesized by solid state reaction method. No peak related to the elemental Sm, Li or any complex compound is found which may be due to their low concentrations [21]. The crystallite (or grain) size of ZnS: Sm, Li particles was estimated using the Scherer's formula [1].

$$D = \frac{0.94\lambda}{\beta Cos\theta} \tag{1}$$

where β is full width at half maxima [FWHM in radians], λ is the X-ray wavelength and θ is the Bragg's angle.
For the estimation of micro strain (μ), we have used the following relation [2]

$$\mu = (\beta \cot\theta)/4 \tag{2}$$

where β and μ have their usual meanings.
The average grain size and micro strain (μ) of ZnS: Sm, Li are found to be 38.9μm and 0.0325 respectively.

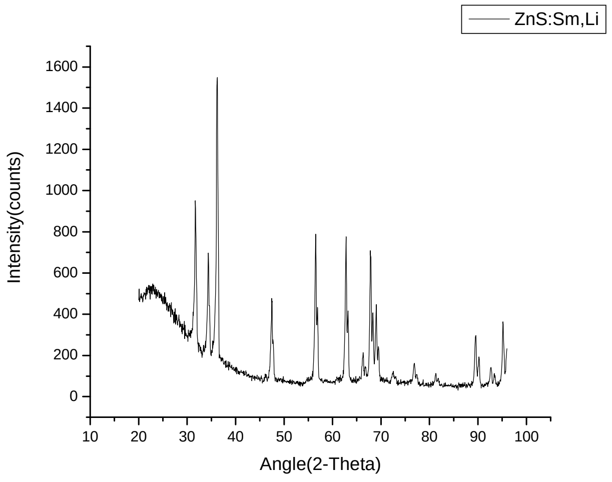

Fig. 1. XRD pattern of ZnS:Sm,Li

3.2 Electroluminescence study

3.2.1 Voltage dependence

The variation of EL brightness of different samples as function of applied voltage at fixed frequencies of 4.5 kHz and 35 kHz is shown in figure 2a and figure 2b respectively. A plot of logB versus $100/V^{1/2}$ is found to be straight line for all the samples as shown in figure 2a and figure 2b. All the samples have been found to obey the universal law $B = B_0 e^{(\frac{-b}{\sqrt{V}})}$ where B is the brightness, V is the applied voltage, and B_0 and b are the constants determined by the particle size of the phosphor, structure of the device and excitation conditions. The slope of curve is slightly increased at higher frequencies of excitation as shown in table1.This can be explained by the increasing chances of excitation with increasing frequency. ZnS: Sm, Li is noticed to reduce EL intensity as compared to ZnS: Cu, Li which may be attributed to lower solubility of Sm as compared to Cu. It is also found that Li in ZnS:Sm,Li enhances EL intensity as compared to ZnS:Sm which may be due to better solubility of Sm as Li plays the role of charge compensator[19,20,21].

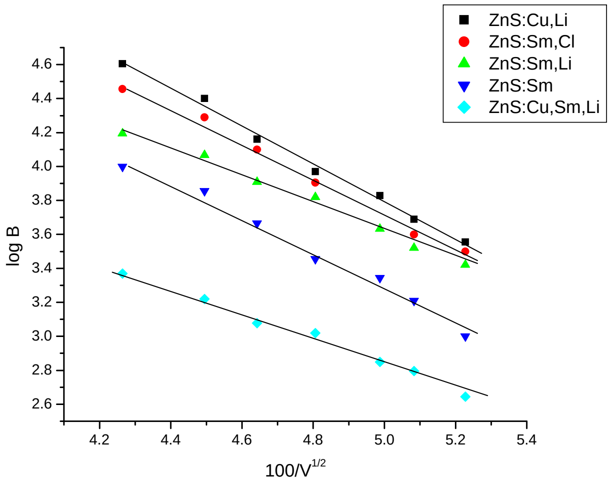

Fig 2a: Voltage dependence of EL brightness at 4.5 KHz

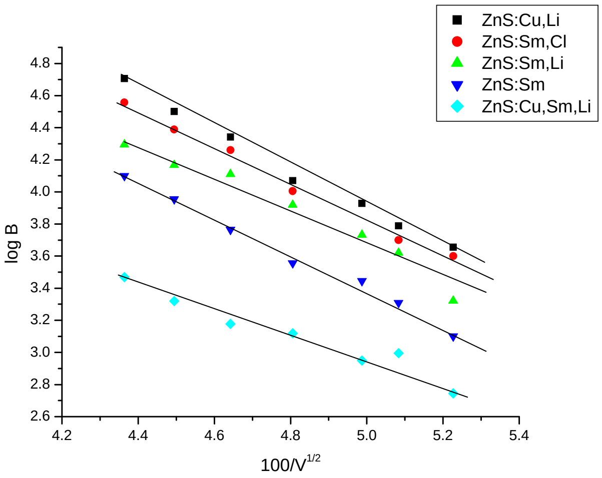

Fig 2a: Voltage dependence of EL brightness at 35 KHz

Table 1

	At	4.5KHz	At	35KHz
	m	c	m	c
ZnS:Cu,Li	-1.11044	9.34489	-1.21246	9.96215
ZnS:Sm,	-1.04352	8.93493	-1.1371	9.50876
ZnS:Sm,Cl	-1.03551	8.46106	-1.06364	8.98703
ZnS:Sm,Li	-0.8308	7.77133	-1.11765	8.97018
ZnS:Cu,Sm,Li	-0.73426	6.51089	-0.74227	6.67411

3.2.2 Frequency dependence:

The frequency variation of EL brightness of different samples is shown in figure 3a and 3b where applied voltage is 360volts and 550 volts respectively. A plot of 1/B versus 1/f is found to be a straight line for all the samples as evident from the figures. All the samples are found to obey the universal law of frequency dependence, $\frac{1}{B}=\frac{1}{\alpha}+\frac{\beta}{f}$ where B is the brightness, f is the frequency and α, β are the constants. However with increasing frequency the change in intensity is rather fast at higher voltages as compared to lower voltages which may be attributed to higher electric field at higher applied voltage

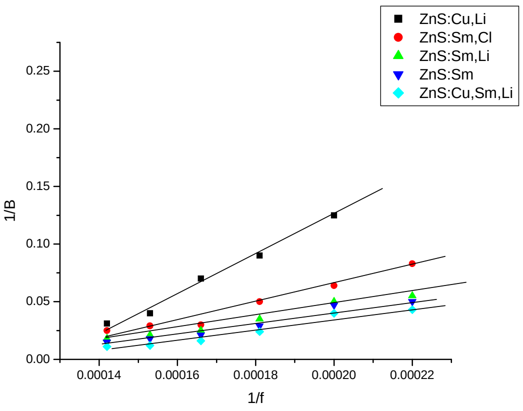

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Fig. 3a: Frequency dependence of EL brightness at 360Volts

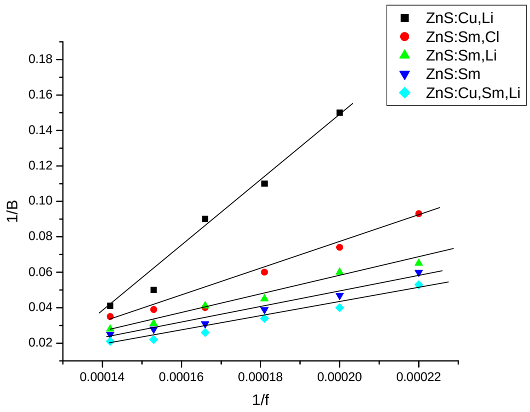

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Fig. 3b: Frequency dependence of EL brightness at 550 Volts

3.2.3 Spectral analysis:

The EL spectra at excitation frequencies 4.5 KHz and 35 KHz are shown in figure 4a and 4b respectively where the peaks have been normalized. In both the cases it is found that the peak emission lies at about 5000A^0 in green region which indicates that the excitation mechanism remains unchanged with increasing frequency. The band transition of rare earth activated phosphors may be attributed to combination of trivalent rare earth with a defect [22]. No intraband transition of Sm is observed due to preparation conditions. Only reducing atmosphere favours intraband transition. [18].It is also observed that ZnS: Cu, Li has broader emission band as compared to Zns: Sm, Li which may be attributed to change in lattice structure. The emission bands for all the samples are found to remain unchanged with excitation frequency as sharp transition levels are involved [23].

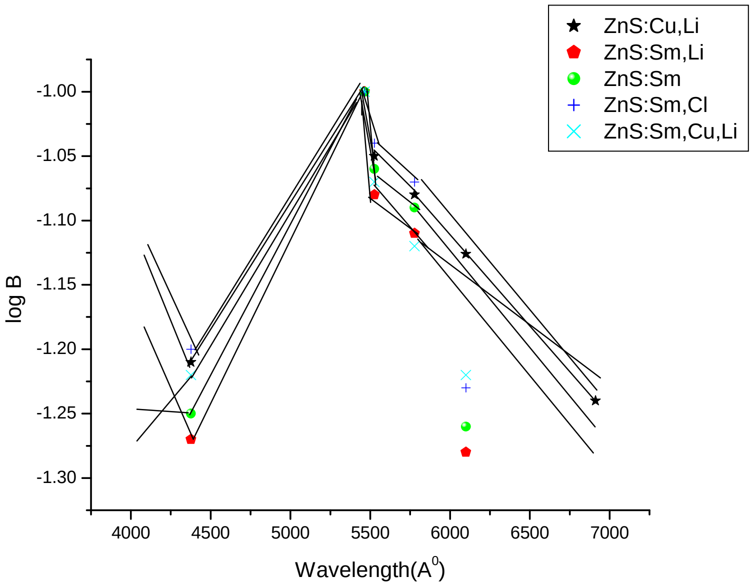

Fig. 4a: Electroluminescence spectral distribution at 4.5 KHz

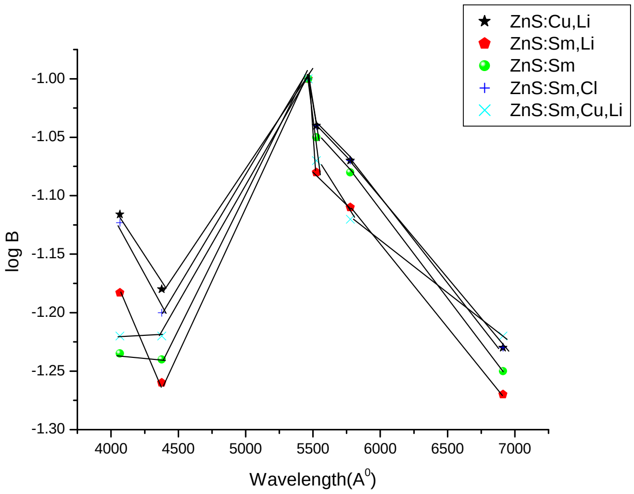

Fig. 4b: Electroluminescence spectral distribution at 35 KHz

4. Conclusions

The lithium incorporation in ZnS: Sm has been tried out by solid state reaction method. Incorporation of Li in ZnS: Sm is found to enhance EL intensity. The emission bands remain unchanged with excitation frequency for all the samples. Doping of Sm in ZnS as activator tends to narrow the band as compared to Cu. The Sm is also noticed to reduce EL intensity as compared to Cu, however, no intraband transition of Sm is observed due to preparation conditions. The reduced EL intensity of ZnS: Sm, Li as compared to ZnS: Cu, Li is due to lower solubility of Sm as compared to Cu.

Acknowledgement

The authors are thankful to Dr. A.C Pandey for providing XRD measurements at Nanophosphor Application centre, University of Allahabad. The author Rajneesh K. Srivastava is thankful to UGC for its financial assistance in form of a project.

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