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Studies on the thermoluminescence glow curves of Mn doped ZnS nanoparticles

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Abstract
This paper reports the synthesis of ZnS nanoparticles doped with Mn using mercaptoethanol (ME) as the capping agent. The particle size of such nanoparticles were measured by X-ray diffraction technique (XRD) and by the Transmission electron microscopy (TEM) patterns and were found to be in between 2nm - 6nm. For the samples with different concentration of the capping agent, it was found that the thermoluminescence (TL) intensity of ZnS:Mn nanoparticles increased as the particle sizes were decreased. The shift in peak position of TL glow curve was also seen with decreasing particle size.

Keywords: Nanoparticles; XRD, TEM, Thermoluminescence, and ZnS.

INTRODUCTION

Thermoluminescence (TL) is defined as the emission of light from a semiconductor or an insulator when it is heated, due to the previous absorption of energy from irradiation. Whenever a semiconductor is irradiated, electrons and holes are created. If electron–hole pairs recombine immediately and emit a photon that is known as fluorescence and if the electrons and holes created do not recombine rapidly, but are trapped in some metastable states separately, they need energy to be released from the traps and recombine to give luminescence. If the detrapping process is caused by heating or thermostimulation, the luminescence is called thermoluminescence. Thermoluminescence (TL) is a well-established technique widely used in dosimetric and dating applications. Thermoluminescence is one of the most important methods to reveal the energy structure and surface states of the semiconductor nanoparticles [1]. As the particles become smaller, the surface/volume ratio and the surface states increase rapidly, thus, reducing the excitonic emission via nonradiative surface recombination [2]. So the surface states are very important to the physical properties, especially the optical properties, of the nanoparticles. Some reports stated that the trapped surface luminescence shifts to the blue as the size is decreased. This paper also reports the similar results.

ZnS is one of the well known II–VI compound semiconductors suitable to be used as host matrix for large variety of dopants because of its wide direct energy band gap (3.7 eV). It is known that ZnS phosphors have a broadband luminescence from the near ultraviolet (UV) to the near infrared (IR). Therefore, it has been often used in the field of optoelectronic devices, such as for light emitting diodes and flat-panel displays. Especially, when ZnS is doped with a small amount of metallic ions, such as Mn and Cu ions, it emits a light in the visible region which is characteristic for the incorporated impurity. Therefore, it forms a very important class of phosphors for the fabrication of electroluminescent devices.

This paper reports the variation of TL intensity with the particle size of the Mn doped ZnS nanoparticles.

EXPERIMENTAL

The powder of ZnS nanoparticles were prepared by using chemical deposition technique described by Khosravi [3]. For synthesis, the 1M aqueous solution of $ZnCl_2$ and 1M aqueous solution of Na_2S were mixed in presence of various concentrations of the capping agent mercaptoethenol (ME). $MnCl_2$ was also mixed in the solution in ratio 99:1, while stirring the solution continuously. The obtained precipitate was washed thoroughly three to four times in double distilled water and then separated by centrifuge at 3500 rpm, and finally air dried. Samples with different concentration of the capping agent and with different concentration of Mn were prepared. Special care was taken to maintain the same physical condition during the synthesis of the sample.

The morphologies and sizes of the mercaptoethanol capped ZnS:Mn were determined by X-ray diffraction studies with Cu Kα radiation (λ=1.5418 Å). XRD data were collected over the range 20^0-70^0 at room temperature. X-ray diffraction patterns have been obtained by Rigaku Rotating Anode (H-3R) diffractometer. The particle size was calculated using the Debye-Scherrer formula. Tecnai 20 G2 (FEI make) Transmission Electron Microscope was used to take the TEM photograph.

The TL glow curves were plotted between emitted light intensity and the temperature of the sample by the help of TLD Reader TL 1009 (Nucleonix) in which heating rate was fixed at 10^0C/sec.

RESULTS AND DISCUSSIONS

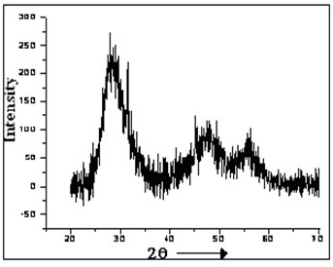

Fig 1. XRD pattern of ZnS:Mn nanoparticles.

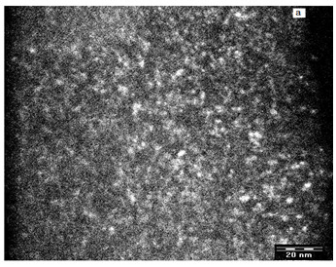

Fig. 2 TEM image of ZnS:Mn nanoparticles.

The XRD patterns for the samples are shown in Figure 1.Three different peaks are obtained at 2θ values of 29.50^0, 48.80^0 and 57.80^0. This shows that the samples have zinc blende structure. The XRD peaks correspond to Bragg diffraction was at (111), (220) and (311) planes for cubic ZnS. Due to size effect, the XRD peak tends to broaden. The broadening of peaks indicates nanocrystalline

behavior of the particles. The width of the peak increases as the size of the particle decreases. The size of the particles has been computed from the width of first peak using Debye Scherrer formula [4]. The particle sizes of the ZnS samples were found to be 2-6 nm.

Figure 1 shows the TEM image of the synthesized Mn doped ZnS nanoparticle. It shows that the particles are not spherical. The particle sizes measured by the TEM images are in the range of 2nm to 6nm.

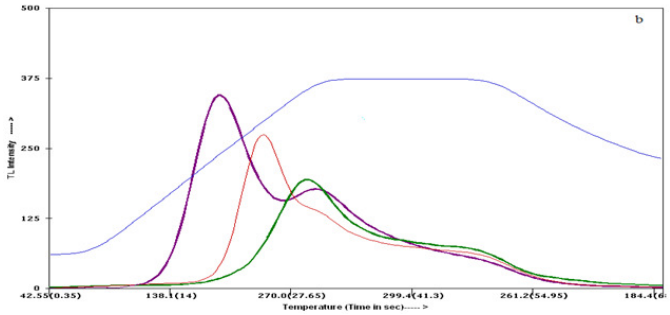

Fig 2. TL glow curves of Mn doped ZnS nanoparticles

The fig 2 shows the TL glow curve of the three samples with different concentration of ME. The concentration of capping agent, peak position, peak intensity, particle size of the samples, the frequency factor, order of kinetics and the activation energy by half width method is given in table 1.

Table 1.

Concentration of the capping agent	Peak position (°C)	Peak Intensity (arb units)	Particle size (nm)	Activation energy electron volt (eV)	Frequency factor S (s^{-1})	Order of Kinetics (b)
5drop	280.3	195	5.30 nm	0.828 eV	8.44×10^{9}	1
10 drop	250.5	260	3.20 nm	0.756 eV	5.12×10^{8}	1
20 drop	159.4	365	2.20 nm	0.728eV	3.18×10^{8}	1

All the samples were irradiated by UV radiation for 5 minutes. The concentration of Mn for all the samples was kept constant at 2% of weight. The peak intensities of the ZnS:Mn nanoparticles varied approximately between 195- 365 unit and the peak position were between 280.3°C-159.4°C. Figures clearly show that the peak intensity increases with increasing concentration of the capping agent. The peak position also shifted towards the lower temperature range with the increasing concentration of the capping agent. As due to the increase in the capping agent concentration the particle size is decreased, hence it can be inferred that the peak intensity increased with decreasing particle size of ZnS:Mn nanoparticles and the peak position also shifted towards the lower temperature with the decrease in the particle size. The TL glow curves are caused by the trapped carriers which are produced during the sample processing. In nanoparticles, as the particles become smaller, ions at the surface increase rapidly. Most ions at the surface are not saturated in coordination. The excited electrons or holes are trapped at surface states located in the forbidden gap. When the sample is heated the detrapping of electrons and their subsequent recombination with holes gives rise to the light emission.

CONCLUSIONS

The nanoparticles of ZnS were grown by chemical routs technique. These nanoparticles were doped by Mn and capped by mercaptoethanol. The study of XRD pattern reveals that the synthesized ZnS particles are in nano range. The particle size of the sample of ZnS was measured in the range 2-6 nm. The TEM results also confirm the particle size to be in the same range as calculated by XRD. The TL glow peak curve shows the change in intensity and change in the peak position with the change in the particle size.

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