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Thermoluminescence of ZnS and ZnS:Mn nanoparticles

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Abstract

This paper reports the thermoluminescence (TL) of ZnS and ZnS:Mn nanoparticles. The ZnS and ZnS:Mn nanoparticles were synthesized using chemical precipitation method, in which mercaptoethanol was used as the capping agent. The particles size of such nanocrystals measured using XRD was found to be in between 2 nm to 3 nm. In the ZnS and ZnS:Mn nanoparticles, the TL intensity increases as the particle size is decreased. The consistency of the size dependence of the TL with that of the surface fluorescence indicates that the TL may be related to the surface states. Smaller particles have higher surface/volume ratio and more surface states, therefore contain more accessible carriers for TL. These two effects may make the TL increase upon decreasing size of the particles.

Keywords:Thermoluminescence,ZnS,ZnS:Mn,Nanoparticles,

1.INTRODUCTION

The semiconductor nanoparticles in the group II-VI have been studied extensively due to their intriguing physical properties compared to their bulk counter parts .Optical properties of such materials can be tuned due to quantum size effects which effectively lead to a size-dependent variation of band gap. Among the most studied II-VI semiconductors are, ZnO, CdS, ZnS, and so far their wide range of luminescence emissions take place from ultraviolet to infrared regions. ZnS is a yellow emitting direct band gap semiconductor of energy gap 3.6eV with low phonon energy suitable in display devices and lighting applications. In the case of nanomaterials, the surface-to-volume ratio is large resulting in larger concentrations of surface states. The surface states are responsible for the production of TL glow curves. Chen et.al.[1] have recorded TL glow curves in ZnS nanoparticle prior to irradiation. They also have observed that the TL intensity increases with the decrease of particle sizes and concluded that the surface ions on the nanoparticles were responsible for the production of TL glow curves. The present paper reports the thermoluminescence (TL) of ZnS and ZnS:Mn nanoparticles .

2. MATERIALS AND METHODOLOGY

The most important step in the studies of nanoparticles is their synthesis. The chemical precipitation method is used in present investigation. The powder of ZnS nanoparticles was prepared by precipitation technique by Khosravi et.al [2]. For synthesis of ZnS nanoparticles, 1M aqueous solution of $ZnCl_2$ and 1 M aqueous solution of Na_2S were mixed and for synthesis of ZnS:Mn nanoparticles 1M aqueous solution of $ZnCl_2$ and 1 M aqueous solution of Na_2S were mixed in presence of various concentrations of mercaptoethanol solution . $MnCl_2$ was also mixed in the ratio 99:1, while stirring the solution continuously . ZnS was prepared by changing 0M and 0.005M capping agent concentration and five different samples ZnS:Mn-I, ZnS:Mn-II, ZnS:Mn-III, ZnS:Mn-IV, ZnS:Mn-V,were prepared by changing the capping agent concentration 0 M, .005 M, .01 M, .015 M,.025 M, respectively. The obtained precipitate was washed thoroughly three to four times in double distilled water and they were separated by centrifugation at 3500 rpm and finally air dried. 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 and ZnS:Mn nanoparticles were determined by X-ray diffraction studies with Cu Ka radiation (λ=1.5418Å). XRD data were collected over the range 20-70^0 at room temperature. X-ray diffraction patterns were obtained using a Rigaku Rotating Anode (H-3R) diffractometer. The particle size was calculated using the Debye-Scherrer formula.

The thermoluminescence was recorded with the help of a TLD reader in which the rate was 59^0C/min. The model of reader is TL 1009I and its make is NUCLEONIX.

3. RUSELTS AND DISCUSSION

The XRD patterns for the samples are shown in Fig. 1(a), 1(b) and 1(c) .Three different peaks are obtained at $2\boldsymbol{\theta}$ values of sample. This shows that the samples have the zinc blende structure and the peaks correspond to diffraction at (1 1 1), (2 2 0), and (3 1 1) planes, respectively [3]. The size of the particles has been computed from the width of the first peak using the Debye-Scharrer formula [4].

$$D = K\lambda / \beta \cos\theta \qquad \text{.....(1)}$$

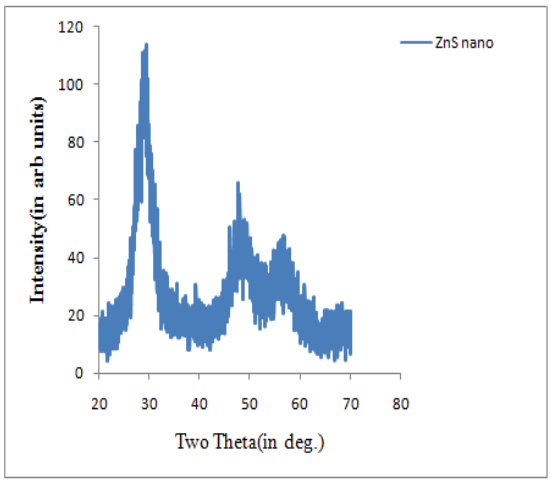

Fig. 1(a) XRD pattern of ZnS nanoparticles

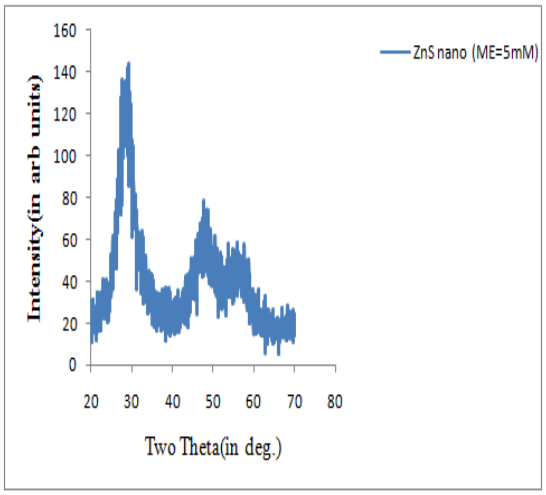

Fig. 1(b) shows the XRD pattern of ZnS nanoparticles with capping agent concentration of merceptoethanol .

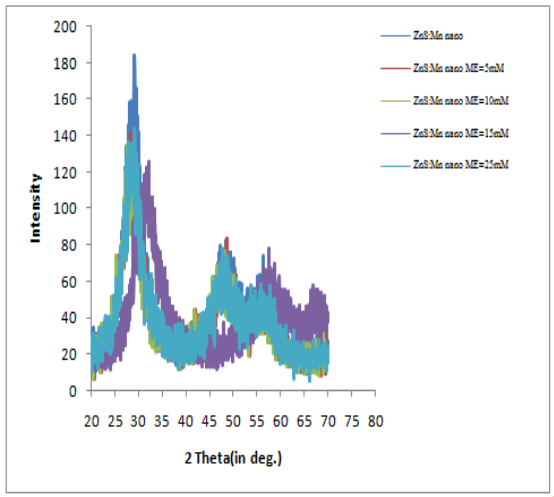

Fig.1(c) XRD pattern of ZnS:Mn nanoparticles and ZnS:Mn nanoaprticles with capping agent concentration of merceptoethanol

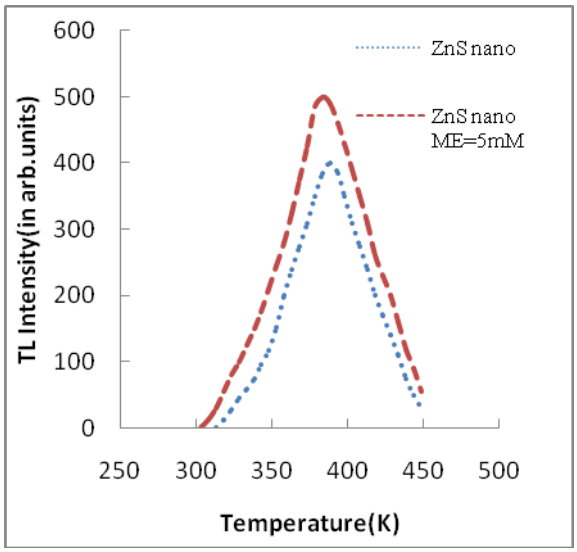

Fig. 2 Glow curve of ZnS nanoparticles with different capping agent concentration of mercaptoethanol .

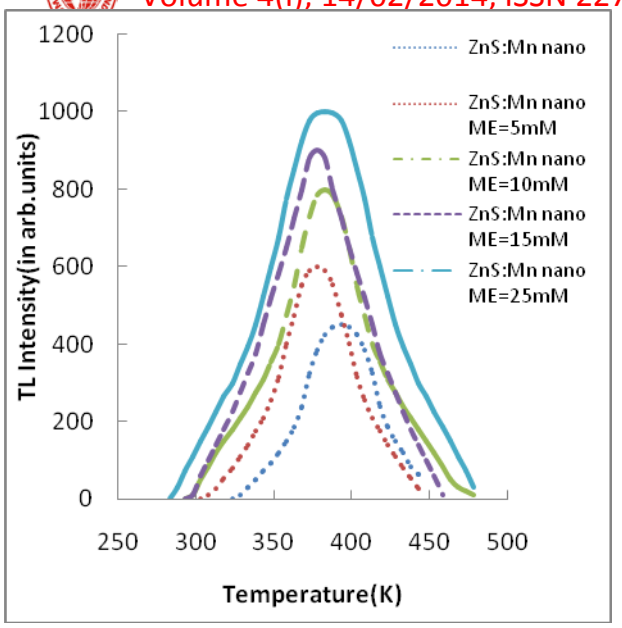

Fig.3 Glow curve of ZnS:Mn nanoparticles with different capping agent concentration of mercaptoethanol

Fig. 2 shows the thermoluminescence (TL) glow curve of ZnS and merceptoethenol capped ZnS nanoparticles. It is seen that the TL intensity of merceptoethenol capped ZnS nanoparticles is higher as compared to ZnS nanoparticles prepared without capping. Fig. 3 shows that the TL intensity of ZnS:Mn nanoparticles increases with the increase in the concentration of capping agent. As the particle size decreases with increasing concentration of the capping agent, its seems that the TL intensity increases as the particle size is decreased. The consistency of the size dependence of the TL with that of the surface fluorescence indicates that the TL may be related to the surface states. TL may be caused by the recombination of carriers released from the surface states or defect sites by heating. Smaller particles have higher surface/volume ratio and more surface states, therefore contain more accessible carriers for TL. Besides, the carrier recombination rate increases upon decreasing size due to the increase of the overlap between the electron and hole wave functions. These two effects may make the TL increase upon decreasing size of the particles. The appearance of TL prior to any radiation reveals that trapped carriers were pre-existed. The investigation of TL may provide some useful information about the surface states that may explain the size dependence of the surface fluorescence.

4. CONCLUSION

The nanoparticles of ZnS and ZnS:Mn were grown by the chemical route in which mercaptoethanol was used as a capping agent. The XRD patterns indicated the growth of the nanoparticles.The sizes of the nanocrystals were found to be 2-3nm.The measurement of TL glow curve suggests the trapping of electrons during the growth of nanoparticles, and therefore, non-irradiated nanoparticles exhibit TL. As the size becomes smaller, the surface to volume ratio increases, and consequently the smaller particles contain more accessible carriers for TL. Another factor is the increase of the carrier recombination rate with decreasing size due to the increase of the overlap between the electron and the hole wave functions.

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