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Red light emission and antimicrobial activities of Mn Doped ZnS Nanophosphor

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Abstract : In this work $Zn_{1-x}Mn_xS$ (x =0, 0.02, 0.05) nanoparticles were prepared by precipitation method at room temperature. The cubic structure of the sample was identified from the X-ray powder diffraction patterns and the average crystallite size is decreases on Manganese doping as compared to undoped ZnSwhich is confirmed by field emission scanning electron microscope. Photoluminescence spectrum infers that the increase in Mn concentration leads to increase in redemission. In addition, the detailed study of both (gram positive, gram negative) bacteria andantifungal activity of the prepared nanoparticles were tested for its efficiency.
Keywords : ZnSnanoparticles, Crystal structure, microstructure, Photoluminescence, antimicrobial activity

1. Introduction

Recently, inorganic semiconductor materials dominate the new generation of fluorescent materials in the light emitting diode and polymer laser devices in commercial market [1].Among the family of II-VI semiconductors for example ZnS, CdS, ZnO, CdTe etc., ZnS is the fore most candidate because of their favorable electronic and optical properties for optoelectronic applications. ZnS nanoparticles are often used as phosphors for display devices[2]. Owing to its wide band gap 3.6 eV at ambient temperature it can be used as a Light emitting diode in the blue to ultraviolet spectral in optoelectronic device applications [3].It is more suitable for UV light based devices such as sensors or photodetectors.Transition metals of wide band gap compounds such as (Cr, Mn, Fe, Co, Ni and Cu); Mn can enhance photoluminescence property of ZnS nanoparticles compared to bulk material. The photoluminescence efficiency and band gap energy of Mn doped ZnS nanoparticles are higher than its counterpart of bulk ZnS: Mn[4].Recently Mn -doped ZnS nanocrystals have attracted much more attention because this material can be used as efficient phosphors, bio-imaging applications,nano tuneddevices, down-shifters and solar cells [5-7].Metals have been used for centuries as bactericidal agents; silver, copper, gold, titanium, and zinc have attracted particular attention, each having various properties and spectra of activity[8].The inorganic nanoparticles gain significant importance than organic due to their ability to withstand adverse processing conditions [9].In the past few years the growing emergence of antimicrobial resistance are major concerns to the public health and scientific communities worldwide in the field of multidrug-resistant bacteria and fungi [10].The antibacterial, antifungal, and antiviral actions of sulfide nanoparticles have been broadly investigated in comparison with other metals. Nowadays integrated powdered zinc salts used for control the development of dental plaque in tooth paste[11].Generally, the antimicrobial activity of the nanoparticles depend on their composition, surface modification, intrinsic properties, and the type of microorganism [12-13].Antimicrobial activity of ZnS nanoparticles and Mn doped ZnO have alreadybeen reported[11, 14, 15, 16].But, to the best of our knowledgewe are first to report the antimicrobial activities of Mn doped ZnS nanoparticles.There are several methods to synthesize ZnS nanoparticles.The chemical co-precipitation method is simplest method due to its various advantages, such as it is more economical than the other methods, doping of foreign atoms are easily possible at room temperature.

2. Experimental Procedure

2.1 Materials

$Zn_{1-x}Mn_xS$ (x =0, 0.02 and 0.05) nanoparticles were prepared by co-precipitation method at room temperature. At first, 10gm. of zinc sulphate dihydrate was dissolved in 50 ml of distilled water and allows it to stir. Then, 50 ml aqueous solution of sodium sulphide was prepared and added drop wise to the above solution. Poly ethylene glycol is used as a capping agent.Mndoped ZnS nanoparticles were synthesized by using manganese sulphate dihydrate as an additional precursor to the above stock solution.

2.2 Antimicrobial studies

The antimicrobial activity of ZnS and Mn doped ZnS nanoparticles were evaluated against gram positive (Staphylococcus aureus,Bacillus),gram negative (Pseudomonas) and Fungus (Candida albicans)with well diffusion method by culturing the microorganism inMuller Hinton agar.Mueller Hinton Agar was prepared; it was sterile at temperature of 121^0C and 50 pound. After autoclaving medium was poured into a petri plate. Peptone water is inoculated with organisms and to spread evenly on MHA.Well was cut onto MHA media. 10 mg samples dissolve in 10uLadded into a well. It was incubated at 37^0 C for 24 hours .The antimicrobial activity was evidenced by the presence of a zone of inhibition (mm) surrounding the well.

2.3 Instrumentation

X-ray diffraction (XRD) analysis was made using XPERT-PRO with Cu-Kα radiation. The crystallite size of samples was determined by Debye-Scherrer formula.The morphology of the samples was determined by Field Emission Scanning Electron Microscope (FESEM).The photoluminescence spectra of the samples were recorded by using Spectrofluro photometer (Shimadzu RF-5301) with an excitation wavelength of 340 nm at room temperature.

3. Results and Discussion

3.1 Structural Analysis:

X-ray diffraction (XRD) pattern of the ZnS and Mn doped ZnS nanoparticles is shown in (Figure 1).Three broad peaks were observed in the diffractrogram at 2θ values equal to 28.60^0, 47.70^0 and 56.50^0 and assigned the Miller indices of the planes (111), (220) and (311). When Mnconcentration is increased the peaks are seems to increase in broadening. This suggests that the Mn ions substituted into the Zn^{2+} ions site, resulting in reducing the crystallite size [17].The mean crystallite size can be calculated by Scherrer's equation $D=0.9\lambda/\beta \cos\theta$ [18].It was found to be 12.1, 10.97 and 10.49nmfor Undoped, 2% and 5% doped nano particles.

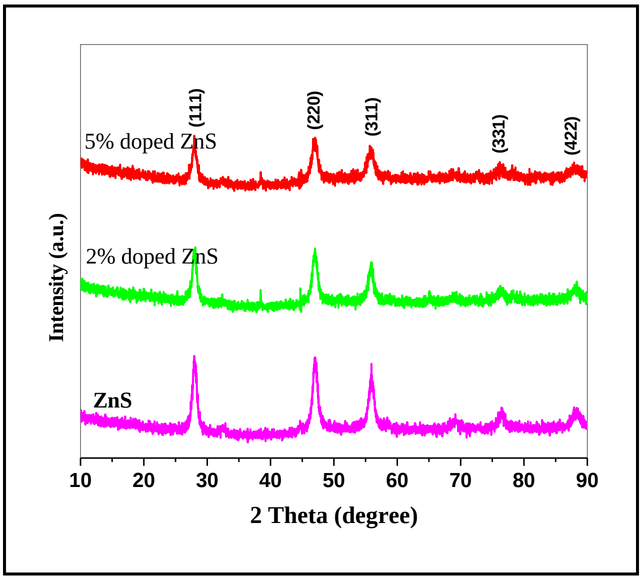

Fig. 1: XRD pattern of Mn doped ZnS nano particles

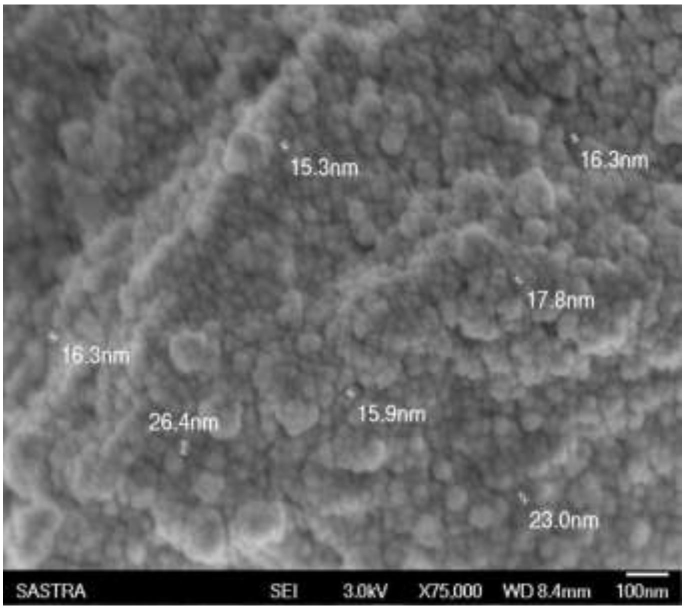

Fig. 2: FESEM image of 5% Mn doped ZnS nanoparticles

3.2 Morphology Analysis-FE-SEM

The surface morphology and particles size of the 5% doped sample are shown in (Figure 2).The particle size is found be 15.3 nm to 26.4 nm. Also the surface morphology of undoped and doped ZnS nanoparticles have spherical shape. In some places, various sizes of the particles (small and large size) are observed, i.e. nano-sized particles seem to be randomly distributed.

3.3PL Studies

Room temperature photoluminescence spectra of Undoped and Mn doped ZnS samples are given in (Figure 3).The emission spectrum of red shift of the photoluminescence peak position at 615 nm has observed[19]. The Mn ion has a d-electron states configuration act as efficient luminescent centers while interacting strongly with s-p electronic states of the ZnS host into which external electronic excitation is normally directed.

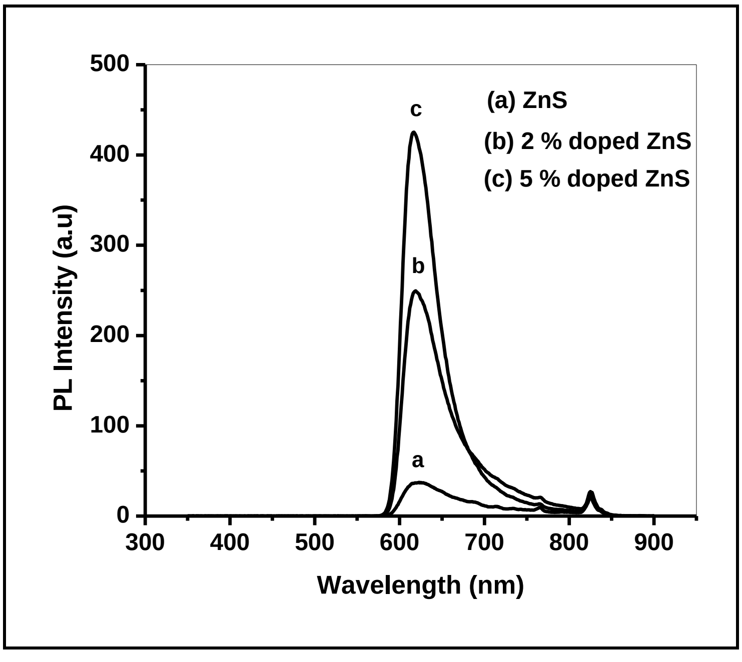

Fig.3: Photoluminescence emission spectra

Fig.4.(a) Pseudomonas

Fig.4.(b) Staph.aureus

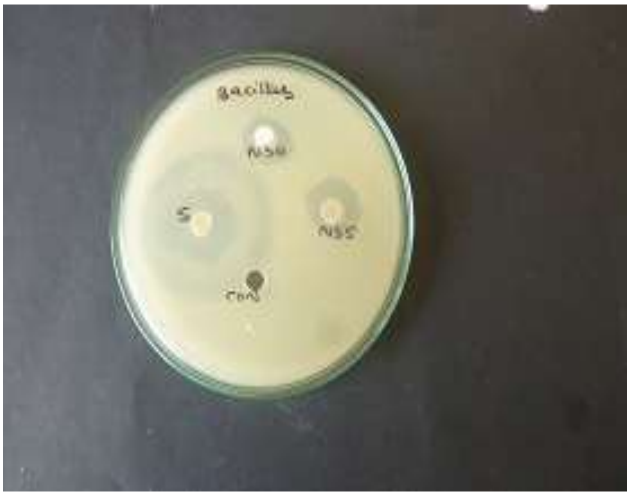

Fig.4.(c) Bacillus

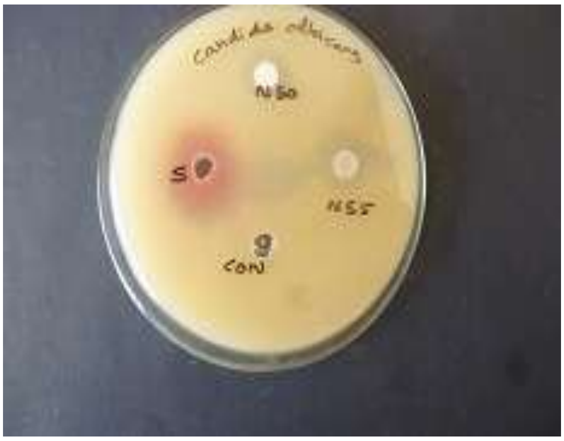

Fig.4.(d) Candida albicans

Fig.4(a),(b),(c),(d) : Antimicrobial activity of ZnS and 5% Mn doped ZnS nanoparticles

3.4Antimicrobial activity

Antimicrobial activity of pure ZnS and Mn doped ZnS nanoparticles at four different microorganisms were studied and is shown in (Figure 4)and their corresponding data are tabulated in Table.1.From the Table.1,ZnS and 5% Mn doped ZnS nanoparticles have produced higher antibacterial activity against Staphylococcus aureus and antifungal activity against Candida albicans at zone inhibition around the well10mm and11mm respectively.ZnS and 5% Mn doped ZnS samples nanoparticles shows lowerantibacterial activity against PseudomonasandBacillusat zone inhibitionaround the well 8mm and 9mm respectively. Investigation on the antibacterial and antifungal activity effect of nanoparticles against Pseudomonas,Staphylococcusaureus,Bacillus and Candida albicans reveals that the 5% Mn doped nanoparticles acts as a strong antibacterial and antifungal activity.

Table.1

Sample code	Pseudomonas (gram negative)	Staphylococcusaureus (gram positive)	Bacillus (gram positive)	Candida Albicans (Fungus)
ZnS (NS0)	8 mm	10 mm	8 mm	10 mm
5% Mn doped ZnS(NS5)	9 mm	11 mm	9 mm	11 mm

Physicochemical properties play an important role in the antimicrobial activity. Ingeneral, smaller particles are more toxic to bacteria such as Pseudomonas,Staphylococcus aureus,Bacillus and fungus (Candida albicans).The antimicrobial activity of ZnS nanoparticles were examined against Bacillus and Candida albicans have been reported already [20, 11].5% Mn doped ZnSnanoparticles shows smaller particle size than pure ZnS nanoparticles, which were confirmed by the XRD result. The diameter of inhibitory circles increased in size for5% Mn doped ZnSnanoparticles.It may be concluded that the advantage of simple inorganic substances acts as antimicrobial agents and may exhibit powerful action even when administered in small amounts because they contain mineral substances essential for human consumption.

4. Conclusions

ZnS nanoparticles with various Mnconcentrations were synthesized byco-precipitation method. The XRD result reveals that ZnS and ZnS: Mn the samples possess the cubic zinc blende structure. PL spectra exhibits emission peaks, which can be attributed to ZnS host and Mn ions respectively. Dueto its lack of absorption in the visible and near IR region is an attractive material for the use of suitable inorganic component to improve the optical properties.ZnS and doped ZnS nanoparticles synthesized by us shows significant antimicrobial activity when tested against gram positive (Staphylococcusaureus, Bacillus), gram negative (Pseudomonas) and Fungus (Candida albicans). Mn doped ZnS nanoparticles has better antimicrobial activity than pure one. From the above studies it is concluded that Mn doped ZnS nanoparticles prepared by the co-precipitation method may be used as promising material in biomedical applications.

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