

## STRUCTURAL AND OPTICAL STUDIES ON $\text{Zn}_{0.98}\text{Mn}_{0.02}\text{S}$ NANOPARTICLES PREPARED BY CHEMICAL ROUTE WITH DIFFERENT CAPPING AGENTS

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In this article we have reported the synthesis, structural and optical studies of zero dimensional nanostructures (nanoparticles) of  $\text{ZnS:Mn}^{2+}$  capped with various organic stabilizers. Zinc acetate dihydride, Manganese acetate tetra hydride and sodium sulfide anhydrous were used as precursors in an aqueous medium to synthesize nanoparticles. The capping agents used were poly vinyl pyrrolidone (PVP), Thiophenol and Thiourea. The nanocrystallite powders were characterized by using x- ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy dispersive analysis of X-rays (EDAX), UV-VIS Spectrophotometer and Photoluminescence (PL) spectrophotometer. The Synthesized nanocrystallites with and without capping agent showed cubic zinc blende structure. The lattice strain and dislocation density were also calculated. The grain sizes estimated from the XRD data are 4.1nm, 2nm, 2.7 nm and 3.7nm respectively. Band gaps of these nanocrystallites were calculated from UV-VIS optical absorption spectra and quantum confinement effect also examined. The photoluminescence properties were studied and the emission peak was observed at 554 nm for all the nanoparticles irrespective of capping agent.

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**Keywords:** Various capping agents,  $\text{ZnMnS}$  nanoparticles, Quantumconfinement, Lattice strain, Dislocation density

### 1. Introduction

Nanomaterials and nanostructures play the important role in applications of nanoscience and nanotechnology in the fields of energy sources, environments, health and medical treatments. The study of nanomaterials and nanostructures is at first place throughout the world. At present nanomaterials and nanotechnology is established as the important branch of science and technology. Day by day nanomaterials are increasingly gaining the attention of not only the scientific community but also the public due to their unique properties, which lead to new and exciting applications. The physical and chemical properties of nanomaterials were exceptionally dependent on the size and shape or morphology [1].

Transition metal doped II-VI semiconductors have been investigated extensively due to their wide range of applications in electroluminescent devices, Light emitting display, optical sensors etc.[2,3].  $\text{ZnS}$  is well known II-VI based wide direct band gap semiconductor with band gap of 3.7eV [4]. Direct and wide band gap semiconducting nanomaterials are potential candidates for applications in nonlinear optics and optoelectronics[5].  $\text{ZnS}$  doped with  $\text{Mn}^{2+}$  ions increases luminescence intensity very much[6]. Among the II-VI semiconductors,  $\text{ZnS}$  is widely studied owing to its stability and technological applications[7]. There are no reports on  $\text{ZnS:Mn}^{2+}$  nanoparticles with different capping agents in systematic comparison of different properties. So

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Manganese doped nanoparticles with different capping agents have been prepared by the chemical route method and the results were discussed in systematic manner. There are several methods for synthesis of nanoparticles however chemical route method is simple and cost effective method. The structure of the synthesized particles is determined by XRD, Surface morphology by SEM, Chemical composition by EDAX, Optical band gap by UV-VIS spectrometer and Photoluminescence studies were carried out.

## 2. Experimental

Manganese doped ZnS nanoparticles were synthesized by a chemical route method without and with different capping agents. Homogeneous solution of zinc acetate, sodium sulphide and manganese acetate solutions were prepared in an aqueous media. 0.1M zinc acetate ( $(\text{CH}_3\text{COO})_2 \text{Zn} \cdot 2\text{H}_2\text{O}$ ) solution, 0.1 M sodium sulphide and 0.1 M manganese acetate ( $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$ ) solution were used for synthesis of  $\text{Zn}_{0.98} \text{Mn}_{0.02}\text{S}$  nanoparticles. Poly(N-vinyl-2 pyrrolidone)(PVP), thiophenol and thiourea were used as the capping agents to control the grains size. First the nanoparticles are prepared without capping agent. Then PVP, Thiophenol and Thiourea were used as capping agent. 0.1M zinc acetate and manganese acetate solutions were added drop by drop into vigorously stirred sodium sulphide solution. The stirring was further allowed for 4 hours at room temperature using a magnetic stirrer. To remove the impurities present in the sample, the particles were washed several times using deionized water. The washed particles were dried under 60 watt lamp for 4-6 hours and finally grinded thoroughly using agate mortar. The as synthesized product was characterized using XRD, SEM, EDAX, UV-VIS Spectrophotometer and photoluminescence studies.

## 3. Results and discussion

### 3.1. SEM studies

The surface morphology of the prepared  $\text{ZnS:Mn}^{2+}$  nanoparticles were studied by SEM(CARL-ZEISS EVO MA 15) and the pictures were shown in Fig.1(a),(b),(c) and (d). The grain sizes of the nanoparticles estimated from the SEM pictures were slightly greater than the grain size obtained from XRD data. This discrepancy may be due to the very small sample area chosen for the SEM scan. From the SEM(fig.1(a)) photographs it was very clear that the nanoparticles without capping agent are agglomerated [8,9], and capped nanoparticles were unagglomerated(fig.1(b),(c),(d)) Especially PVP sample hinders agglomeration very much both sterically and electrostatically, it is shown in fig.1(b). Manoj Sharma et.al also reported the hindering of agglomeration with PVP [8].

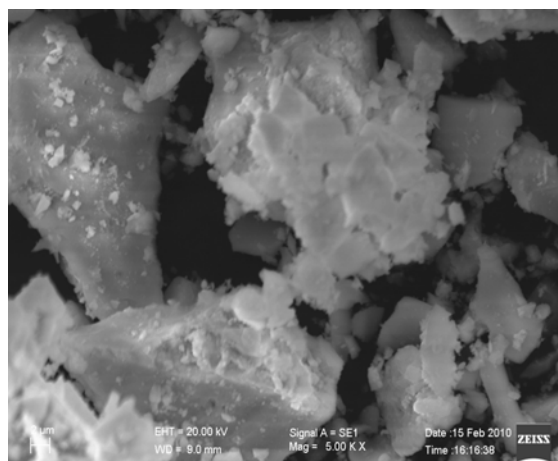


Fig.1 (a)

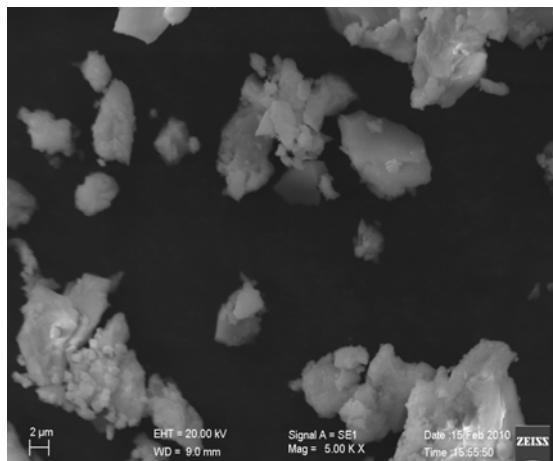


Fig.1 (b)

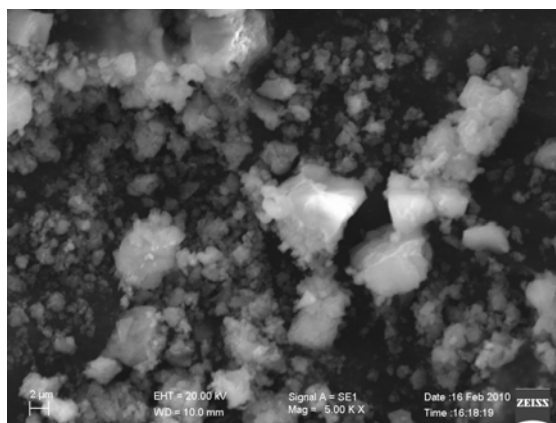


Fig.1(c)

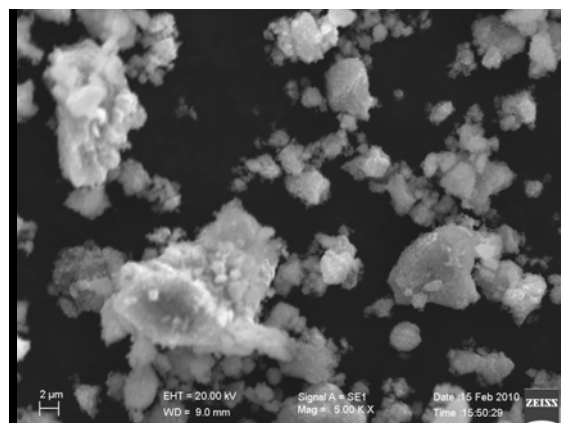


Fig.1 (d)

Fig.1. SEM pictures of  $\text{Zn}_{0.98}\text{Mn}_{0.02}\text{S}$  nanoparticles (a) without capping, (b) with PVP, (c) Thiophenol and (d) Thiourea capped samples.

### 3.2. EDAX analysis

Energy dispersive analysis of X-rays indicated that the presence of Zinc, sulphur and Manganese in all prepared samples. EDAX pattern of  $\text{Zn}_{0.98}\text{Mn}_{0.02}\text{S}$  without any capping agent is shown in fig.2. In thiourea capped sample higher percentage of oxygen is present in the EDAX spectrum. This oxygen may be incorporated into the nanoparticles either from the atmosphere or from the aqueous medium of the solution resulting in higher amount of oxygen contamination [10]. The EDAX analysis shows that the nanoparticles were well stoichiometric with the component of zinc, sulphur and manganese except with thiourea capped sample.

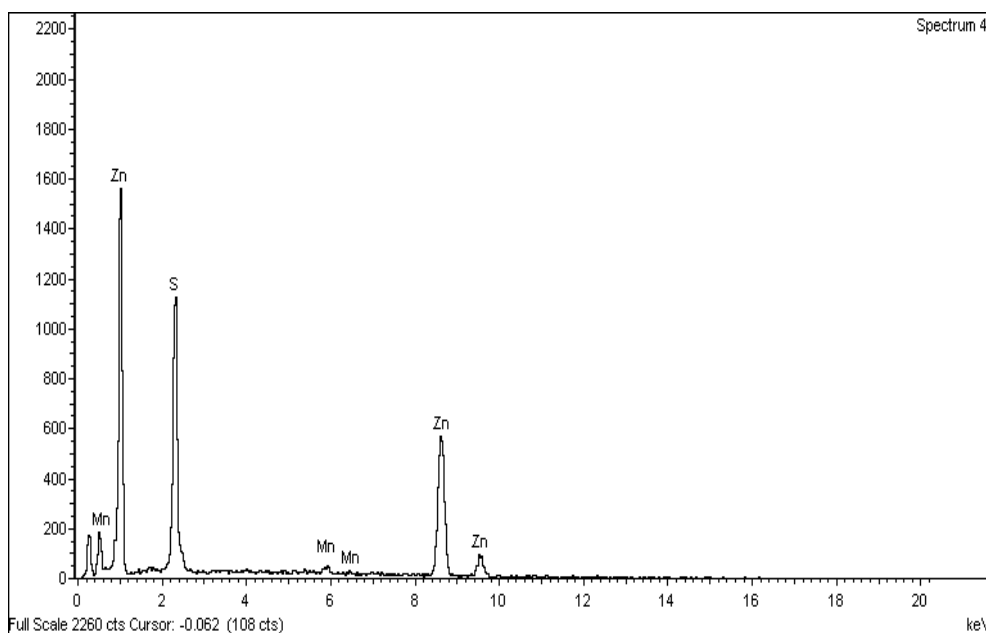


Fig. 2. The EDAX pattern of the  $Zn_{0.98}Mn_{0.02}S$  without capping agent.

Table. 1 EDAX analysis of  $Zn_{0.98}Mn_{0.02}S$  with different capping agents.

| S. No. | Capping agent | Element (Wt %) |      |       |
|--------|---------------|----------------|------|-------|
|        |               | Zn             | Mn   | S     |
| 1.     | No capping    | 62.96          | 1.51 | 35.53 |
| 2.     | Thiourea      | 69.46          | 2.63 | 0.44  |
| 3.     | Thiophenol    | 76.11          | 1.38 | 22.51 |
| 4.     | PVP           | 65.03          | 1.61 | 33.36 |

### 3.3. XRD Studies

The x-ray diffraction (XRD) patterns were recorded in the  $2\theta$  range of  $20^\circ$  to  $70^\circ$  at room temperature, with a step of  $0.03^\circ$  using an x-ray ( $CuK\alpha=1.541\text{\AA}$ , 40kv, 30mA) diffractometer (model Seifert 3003 TT). Based on the XRD patterns the structure and the average crystallite size was determined using the Scherrer's formula

$$D = 0.89\lambda / \beta \cos\theta \quad (1)$$

The XRD pattern of the prepared samples were shown in figure 3(a), (b), (c) and (d). The strong and sharp diffraction peaks indicates that the product was well crystallized and (111), (220) and (311) peaks were common in all samples and it is concluded that the structure is pure cubic zinc blended.[9,11-16]. In thiourea capped sample three unknown peaks were observed and (111) peak is absent, this discrepancy may be due to the high amount of oxygen content present in the sample. The variation of grain size with different capping agents was shown in Table:2, assuming that the grain size is an equivalent term to crystallite size[17]. Thiourea is used as a sulphur source and capping agent. Thiourea can be employed as an excellent sulphur source [18, 19].

Table 2. Comparison of Grain size of nanoparticles with earlier reported values.

| Sample                | Capping agent    | Grain size in nm | Previously reported grain size values in nm |
|-----------------------|------------------|------------------|---|
| $Zn_{0.98}Mn_{0.02}S$ | No capping agent | 4.1              | 3.6 [20]                                    |
|                       | Thiourea         | 3.7              | 20.35 [21]                                  |
|                       | Thiophenol       | 2.7              | 7.2 [22]                                    |
|                       | PVP              | 2.0              | 2.0 [8]                                     |

The lattice parameters were calculated using the equation

$$d = a / \sqrt{h^2 + k^2 + l^2} \quad (2)$$

The lattice parameters were  $5.40\text{\AA}$ ,  $5.38\text{\AA}$ ,  $5.39\text{\AA}$  and  $5.39\text{\AA}$  for all four samples respectively. These values were well matched with the JCPDS value  $5.406\text{\AA}$ . From these results we conclude that PVP was an excellent capping agent to control the grain size. D.Mohan et.al[5] synthesized the ZnS:Mn nanoparticles using polyvinyl alcohol as a capping agent and obtained grain size of 11nm. S.Challammal et.al[23] reported the grain size about 4 nm with ethylene glycol as capping agent. J.Nanda et.al[15] reported the average grain sizes of 1.8nm, 2.5nm and 3.5nm for three samples with thioglycerol as capping agent. K.Matras et.al[24] reported the grain size about 10 nm with cyst amine, combined with hydrophobization capping agent. M.H.Yousefi et.al[16] reported the grain size around 2 nm with mercapto ethanol.

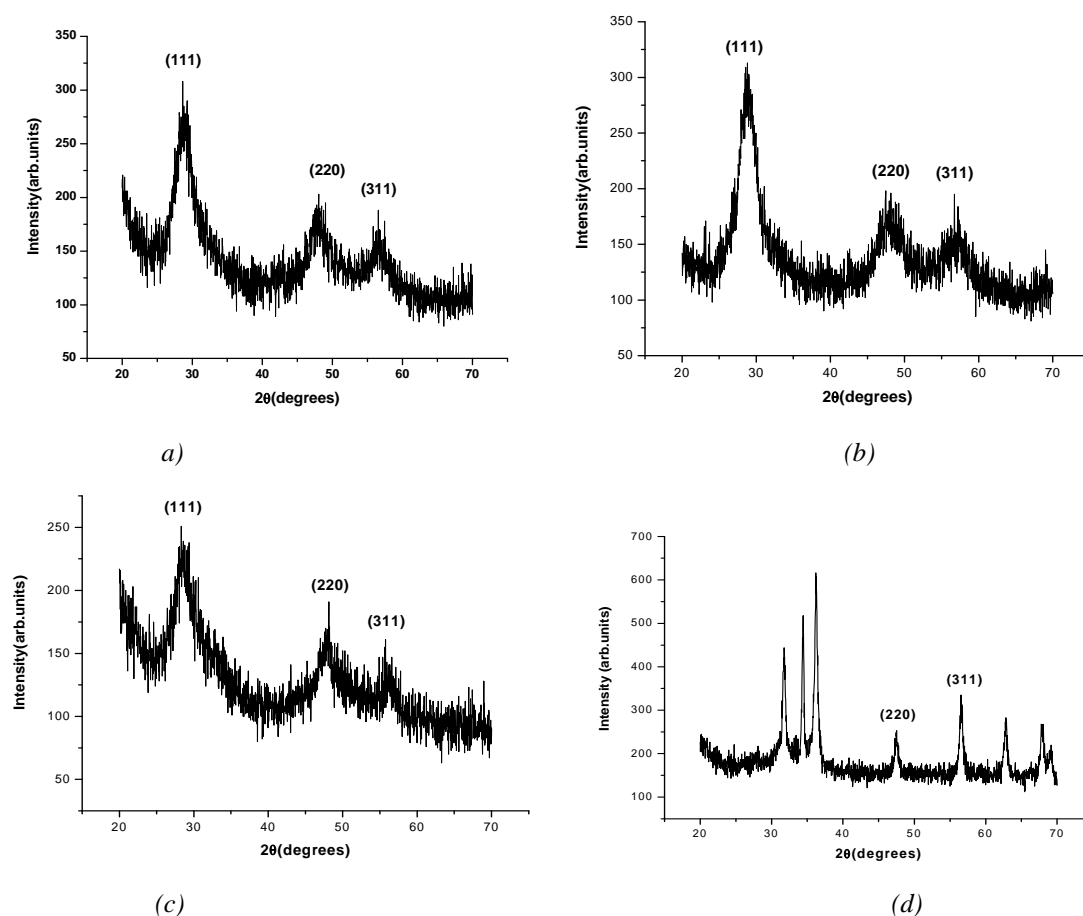


Fig. 3. XRD pattern of  $Zn_{0.98}Mn_{0.02}S$  nanoparticles (a) without capping (b) PVP, (c) Thiophenol and (d) Thiourea capped samples.

The average strain of ZnS:Mn nanoparticles was calculated by stokes –wilson equation

$$\varepsilon_{\text{str}} = \beta / 4 \tan \theta \quad (3)$$

The dislocation density was also calculated from the relation [25]

$$\delta = 15\varepsilon/aD \quad (4)$$

where a= lattice parameter, D= average grain size

The average lattice strain and dislocation density were calculated for all the prepared samples and are shown in Table 3. For all these samples the lattice strain and dislocation density were not changed much. From these values we can concluded that the capping agents does not influences the lattice strain and dislocation density.

Table 3. Lattice strain and dislocation density of as prepared four samples.

| Sample                                      | Capping agent    | Lattice strain<br>$1 \times 10^{-2}$ | Dislocation density $\delta$<br>$1 \times 10^{17}$ lines/m |
|---|------------------|--------------------------------------|--|
| $\text{Zn}_{0.98} \text{Mn}_{0.02}\text{S}$ | No capping agent | 4.8                                  | 5.2  |
|   | Thiourea         | 2.2                                  | 1.13   |
|   | Thiophenol       | 4.8                                  | 4.9  |
|   | PVP              | 4.7                                  | 4.8  |

### 3.4. Optical studies

#### 3.4.1 Optical absorption

The absorption spectra of ZnMnS nanoparticles synthesized with different capping agents were shown in fig.4. From the UV-VIS absorption spectra the bandgap was calculated using the formula

$$E = hc/\lambda \quad (5)$$

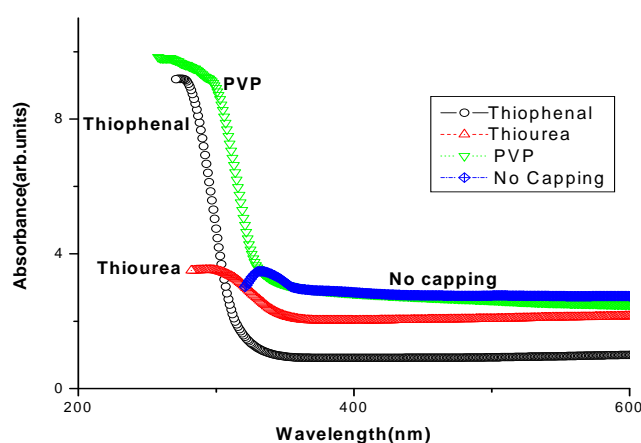


Fig. 4. Optical Absorption Spectra of  $\text{Zn}_{0.98}\text{Mn}_{0.02}\text{S}$  nanoparticles with different capping agents.

The band gap values and corresponding absorption wavelengths are shown in Table.4. From these results we can conclude that as soon as the particles size is reduced the

absorption edge is shifting towards lower wavelength, significant blue shift is observed. The optical absorption confirms the quantum confinement effect of nanoparticles.

Table 4. Optical parameters of as prepared four samples.

| Sample                                     | Capping agent | Band gap of nanoparticles(eV) | Particle size (nm) | Absorption peak (nm) |
|--|---------------|-------------------------------|--------------------|----------------------|
| $\text{Zn}_{0.98}\text{Mn}_{0.02}\text{S}$ | No capping    | 3.88                          | 4.1                | 320                  |
|  | Thiourea      | 4.13                          | 3.7                | 301                  |
|  | Thiophenol    | 4.50                          | 2.7                | 276                  |
|  | PVP           | 4.60                          | 2.0                | 270                  |

### 3.4.2 Photo Luminescence

The room-temperature photoluminescence spectra of as-prepared  $\text{ZnS:Mn}^{2+}$  nanoparticles were shown in figure.5. All the samples were excited at 410 nm and common emission peaks were observed at around 554nm, which indicates the yellow emission [7] in all the samples. The peak at 554 nm is attributed to the  ${}^4\text{T}_1-{}^6\text{A}_1$  transition in the  $\text{Mn}^{2+}$  ions [26]. Here no capping agent effects were observed because all the ligands were washed away after precipitation.

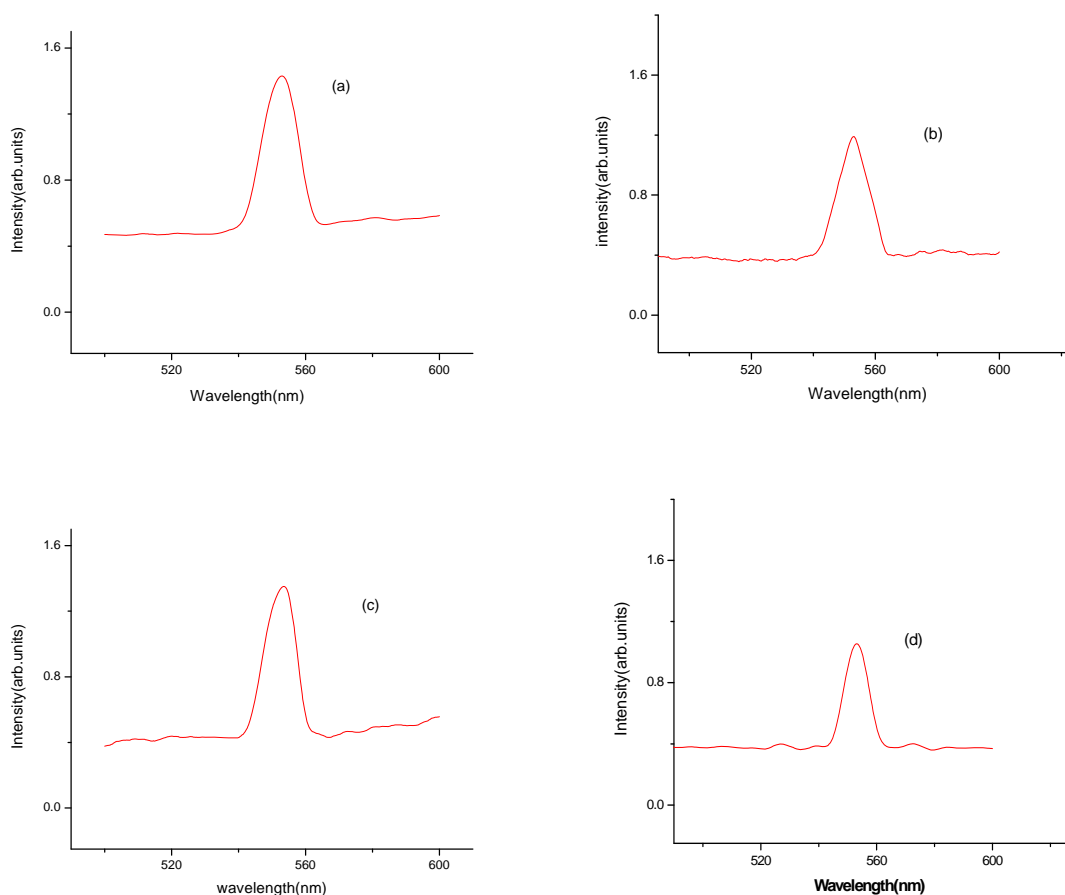


Fig. 5. PL spectra of the  $\text{Zn}_{0.98}\text{Mn}_{0.02}\text{S}$  nanoparticles (a) without capping, (b) with PVP, (c) Thiophenol and (d) Thiourea capped samples.

#### 4. Conclusions

From this work we conclude that the organic stabilizers play an important role in the control of the grain size of the nanoparticles. In this paper we reported the synthesis of the ZnS:Mn nanoparticles without and with (PVP, Thiophenol and Thiourea) capping agents. The average grain sizes obtained are 4.1 nm, 2 nm, 2.7 nm and 3.7 nm respectively. From these results we conclude that PVP is one of the best organic stabilizers. The band gaps calculated increase with decreasing grain size and this confirms the quantum confinement effect of nanoparticles. Without capping agent nanoparticles were agglomerated. Irrespective of capping agent the luminescence peak was obtained at 554 nm in all the samples. This was due to the presence of Mn.

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