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Effect of Synthetic Method and Dopant on Zinc Sulfide Quantum Dots

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Abstract : Nanomaterials synthesis and its application in the field of electronics have increased vastly in the last two decades. There are various methods of synthesis and processing employed in industries to exploit to their production values in its cheapest way. Zinc sulfide is a prominent member of II-IV semiconductor with a verity of applicable properties. A dopant such transition metals have enhanced the optical and electrical properties of the nanoparticles. In the meanwhile, the synthetic ways also act on the properties of nanomaterials. In this method paper, zinc sulfide was synthesized with two different methods using two different dopants. The methods for synthesis were a hydrothermal process and simple wet chemical processes. The dopants selected were manganese and nickel. Each process and dopants increased the ability of materials which were quantified by the means of optic electrical properties and morphology. These properties were analyzed by UV-visible spectroscopy and XRD and FESEM.
Keywords : zinc sulfide; dopant; nickel; manganese; semiconductors.

1. Introduction:

In the recent year's studies on nanomaterials has generated a greater interest. The unique properties, applications have enhanced the number of groups working on it. In the field of electronics, the nanomaterials gave a revolutionary breakthrough such as reduction in size and enhancing the speed and accuracy. Especially in the field of semiconductors, they have created miracles. This is because nano semiconductors show different properties compared to bulk semiconductors [1-5]. They behave differently because of drastic reduction of particle size which results in a change of band structure. Band gap increases as the particle decrease with this, the edge of band splits and create discrete energy levels. Doping of any optically active material will change its electronic structure and transition probability of the host nanoparticles and shows new varieties of emissions in different wavelengths [2]. This depends on the type of impurity, concentration, and crystal dimension. They play very important role in the efficiency and position of emission bands. Thus they act as the catalyst in the field of device developments.

Among several nano semiconductors, Zinc sulfide is an II-VI intrinsic semiconductor with excellent physical properties. The properties such as photoluminescence (PL) electroluminescence (EL) and cathode luminescence (CL) are found to be of greater interest. Wide band gap (3.7eV) at room temperature of this compound is of greater importance in the field of optoelectronics such as ultraviolet light emitting diodes [5-8]. The applications of ZnS in the devices such as window layer of solar cells, in the production of hydrogen blue-green LEDs, electroluminescence displays, anti-reflection coatings for Infrared devices and other nonlinear optical devices. Pure ZnS has an emission at 420-450 nm but the dopants like transition metals and rear metals such as nickel, iron, manganese, copper, *etc* [6-11]. There are several reports that photoluminescence property of

ZnS changes with amount and type of impurities. When the ZnS nanocrystal is doped, the impurities occupy Zn lattice and behave like trap sites for electron and holes[12]. Thus, excited electrons from valence band to conduction band absorb equal or greater energy than the band gap energy by forming a junction.

Greater research can be performed by transporting and controlling various spin states by the presence of Manganese. Manganese allows to change in band gap and other luminance centers by different energy levels, of the 3d electrons with the s-p electronic state of the host[13]. The Mn^{2+} ion exhibits a broad change in the crystal field strength with the host. The emission of color may vary accordingly with $^4T_1$-$^6A_1$transition [5].

In the studies we are presenting here about the comparison between synthetic methods and presence of nickel and manganese in the zinc sulfide could interfere in the optical properties, lattice, and morphology.

2. Experimentation:

Zinc sulfide may be synthesized with many methods like wet chemical method, a sol-gel method, hydrothermal, solvothermal process and thermal evaporation methods, *etc*[4]. For synthesizing the doped ZnS, hydrothermal and chemical process were chosen for Manganese and Nickel respectively. Different processes were chosen for the higher yield and less amount of chemicals and shorter time.

In the hydrothermal process, solutions of zinc acetate, manganese acetate, and thiourea were used. In a high-temperature reaction, these solutions were taken in the acid digester and heated up to 200^0C for 24 hours, cooled, dried and stored for analysis[5].

In the chemical process, to the Zinc acetate solution Nickel chloride and Sodium sulfide were added dropwise for 6 hours. Ash white precipitate was formed which was washed with alcohol and dried at 60^0C. This was stored for further analysis[9].

3. Characterization:

During synthesis of Mn:ZnS, yield was found to be 70% where the amount of raw materials used was 900 mg and the yield obtained was 650 to 655 mg per batch. Similarly, in Ni:ZnS the yield present was high. In the synthesis, the total amount of chemicals used was around 700 mg and the total yield was 500 to 510 mg for every batch. At first, sufficient amount of materials were synthesized and preceded to further analysis.

Materials were characterized for optical and morphological characteristics, using UV-Visible-NIR spectroscopy for the analysis of band gap and average particle size. X-Ray diffraction studies were carried out to analyze the morphology and crystal size, further was confirmed by FESEM.

4. Results and discussions:

4.1. Optical Properties and Particle size:

Both the Manganese doped and Nickel doped ZnS were dispersed in methanol followed by sonication for 10 minutes. This dispersion was analyzed by UV-Visible-NIR spectra using Beckman Coulter DU730 LSUV/Vis spectrophotometer in a quartz cuvette with the path length 10 mm. This was done at room temperature.

The spectrophotometric results are as shown in the fig (1). Both manganese doped and Nickel-doped ZnS showed the characteristic Absorption in UV region that is from 200 to 350 nm but it did not show any absorbance in Visible or NIR range.

The absorption edge at 289 nm is assigned to the characteristic absorption band edge of ZnS nanoparticles, which is blue, shifted as compared with the corresponding bulk band gap (3.90 eV) of ZnS due to quantum confinement effect. However, the position of absorption edge for the Mn:ZnS nanoparticles is gradually blue-shift with increasing the concentration of Manganese. The Direct band gap of the samples was calculated by plotting $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ plot and then extrapolating the straight portion of the curve on the $h\upsilon$

axis at α = 0. The straight lines imply that the Mn:ZnS samples have direct energy band gap and were 3.87 eV. The same shifts of the absorption edge with increasing the Manganese concentration were also reported [14].

In Nickel doped ZnS, this blue shift in the absorption edge was due to the reduction of particle size and band-gap energy was 3.90 eV in Ni:ZnS nanoparticles . It should be noted that the Ni^{2+} ion, with an ionic radius of 0.69 Å was used as a dopant ion with smaller ionic radius than Zn^{2+} ion (0.74Å). Thus, due to the occurrence of the above-mentioned phenomena, the particle size of the Ni:ZnS nanoparticles can be reduced and causes small blue shifts observed in the UV–Vis absorption peaks. The similar blue shifts have already been reported for cobalt, iron, and copper when doped with ZnS nanoparticles[1, 7-11].

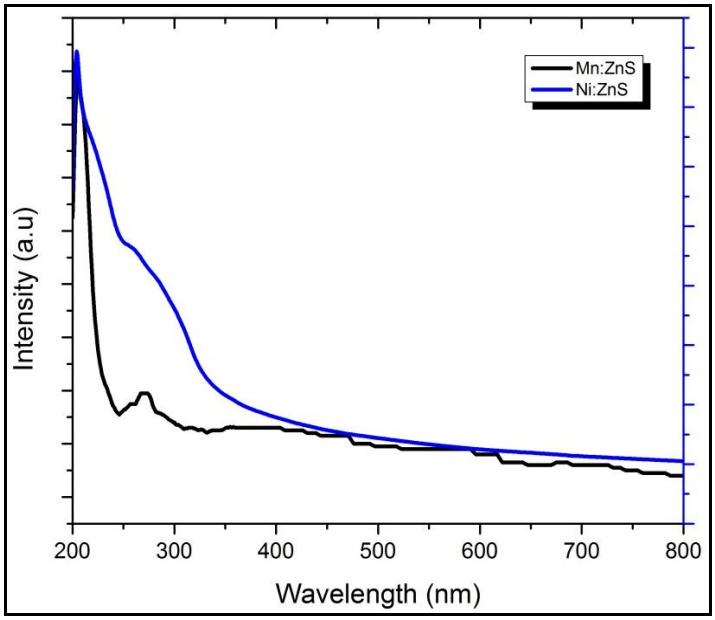

Figure 1 UV-Visible-NIR spectra of Mn:ZnS and Ni:ZnS

By this UV-Vis Spectra, one can calculate the average particle size using the absorbance wavelength with the mathematical model of effective mass approximation. The effective radii of Mn:ZnS and Ni:ZnS were calculated (59 nm and 109 nm respectively).

4.2. Morphology, Crystallinity and Crystal size:

These properties are the texture and the type of crystals occurred in the material, which was characterized by Rigakumini flex-II desktop X-Ray diffractometer with Cu Kα source, operating at 30 mA and 40 KV. The crystallinity and crystal size of Ni:ZnS nanoparticles was determined on the basis of X-ray line broadening and calculated by Debye-Scherrer formula.

X-ray diffraction pattern of ZnS doped with Manganese and Nickel are shown in Figure 2. The patterns indicate that all the samples are consistent with cubic zinc blende structure of ZnS which are in close agreement with the standard ICDD (International Center for Diffraction Data) card number 80-0020. From the XRD patterns, the broadening of the diffraction peaks of the nanoparticles is obvious which reflects the characteristics of nanosized materials. The most prominent peak observed in the figure corresponds to the lattice plane of (1 1 1). Two other peaks corresponding to the lattice plane (2 2 0) and (3 1 1) are observed with varying intensities [5-11]. There is no phase transformation due to Mn^{2+} and Ni^{2+} doping to ZnS host[1, 5].

According to the calculations using Debye-Scherrer formula, the crystalline size of the both Mn:ZnS and Ni:ZnS were 3.10 nm and 3.35 nm, the crystallinity was 46% and 53% respectively.

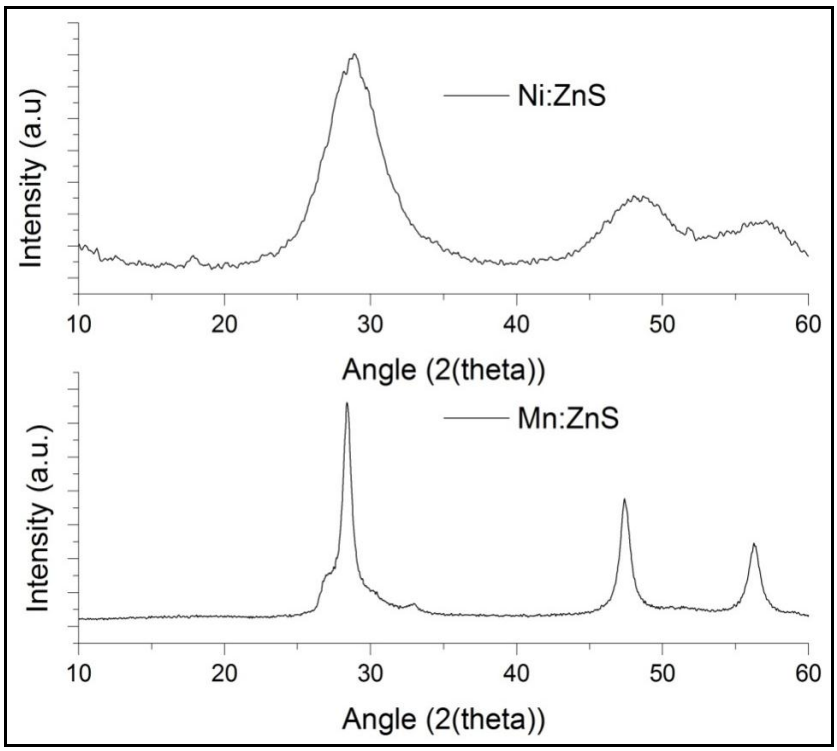

Figure 2 XRD Pattern of Mn:ZnS and Ni:ZnS

4.3. Scanning electron microscopy of Mn:ZnS and Ni:ZnS quantum dots:

Scanning electronic microscopy gives detail information of the surface and the shape of the quantum dots. In figure 3(a) Mn: ZnS dots looks in a spherical shape, embedded in small structures. This shows that the spiracle structure is due to agglomeration of ZnS nanodots. This is because the hydrothermal process has higher temperature and pressure which leads to the formation of quantum dots but the process of cooling will initiate the formation of agglomerates and make them spherical shaped structures.

In figure 3(b) Ni: ZnS quantum dots are shown. Here these are irregular in shape. It is because the process used for is a wet chemical process. As this has no external pressure and the temperature is standard, there will not be any regulating mechanism for shape. But size can be regulated by maintaining the sulfide ion in the solution. The higher the sulfide ion bigger will be shaped. Because of this, the shape of the material is irregular in shape.

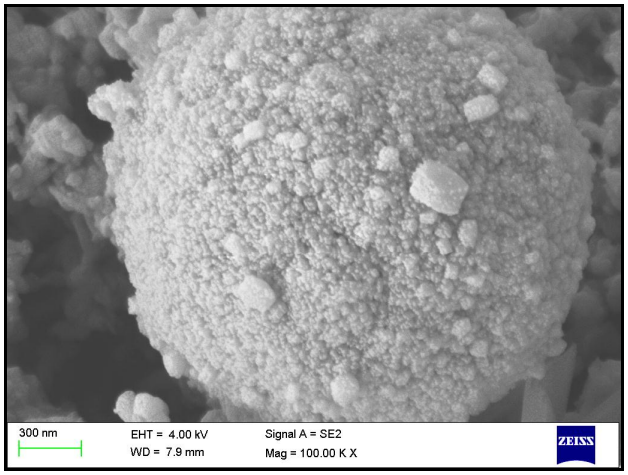

Figure 3(a):FE-SEM image of Mn:ZnS

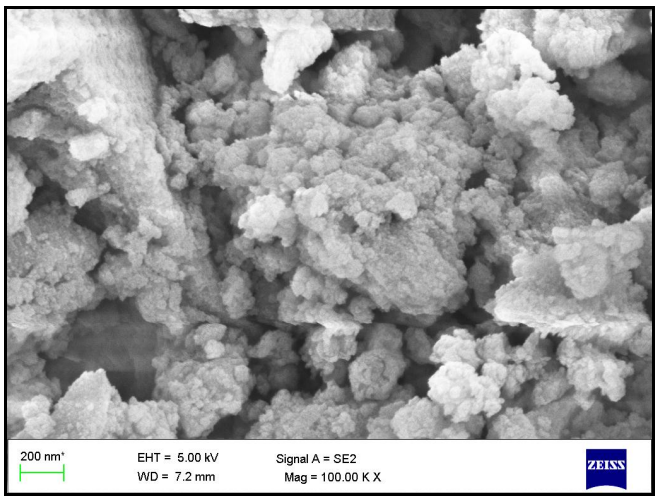

Figure 3(b): scanning electron microgram of Ni:ZnS

5. Conclusion

Zinc sulfide doped with transition metals like Manganese and Nickel have been successfully synthesized by hydrothermal process and wet chemical process respectively for obtaining the higher yield. These were characterized by XRD and UV-Visible spectroscopy. In XRD it revealed that the particle exhibits pure cubical crystal and estimated size were 3.10- 3.35nm. This was then analyzed for optical band gaps (3.87-3.90 eV) which show that the presence of Nickel and Manganese in ZnS lattice will increase the optical properties.

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