Structural and Optical Properties of $Zn_{0.98}T_{0.02}S$ (T=Mn, Cu, Ni, Co, Cr, Cd & Sn)Quantum dots: A Comparative Study

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Abstract .$Zn_{0.98}T_{0.02}S$ (T= Mn, Cr, Cu, Ni, Co, Cd &Sn)quantum dots (QDs) were prepared successfully using co-precipitation method at room temperature. The properties of lightly doped (T = 2 %) ZnS were compared with various transition metal ions doping. The synthesized samples were analyzed using x-ray diffraction study and transmission electron microscopic study. From the structural analysis, it was noted that all the samples were exhibited cubic structure except Cu dopedZnS QDs. The particles size was estimated and they exhibitedwithin the range of 2-3nm. TEM pictures supported for identification of the spherical structure of particles and size of the particles. EDX analysis confirmed the presence of elements in prepared samples. UV- visible absorption and transmission studies evidenced the optical properties of samples. The optical band gap was calculated for each sample and they were in the range of 3.5eV to 4.00eV. The reason for blue shift and red shift on band gap was discussed based on size effects and electron transition between d shells. This comparative analysis will support to the material selection for optoelectronic device fabrication.

INTRODUCTION

Zinc Sulfide is a first semiconductor and it is categorized on wide band gap materials. It exhibits two different structure viz. cubic and wurtzite. The band gap value is 3.7 eV for cubic structure. In II-VI semiconductor group ZnS is being best candidate for solar, optoelectronic device, luminescent label, Field Effect Transistors and spintronic device applications [1]. Tuning of structural and optical properties of ZnS QDs by doping will yield better result for many applications. For tuning the properties, transition metals are playing an important role on ZnS QDs. Mn, Cu, Ni, Co, Cr, Cd, Sn ions were chosen as dopant for the present study.

Incorporation of Mn produced better optical performance in earlier study [2]. Cu, Cr, Ni and Co ions were doped to analyze the structural and magnetic properties of ZnS QDs [3]. Cd and Sn were also added in this list to extend the limit. In the present work, we have monitored the structural and optical performance of ZnS QDs by lightly doping of transition metal ions. Even though there are many methods like hydro thermal, solvo thermal, sonochemical, sol-gel and other methods, co-precipitation method was chosen for synthesis. This method is simple, cost effective and easy for mass production. In this paper we have synthesized the ZnS QDs with various transition metal ions doping and analyzed the structural, optical properties finally compared the results to identify the optimum dopant candidate.

EXPERIMENTAL DETAILS

Sample Preparation

The synthesis of $Zn_{0.98}T_{0.02}S$ (T= Mn, Cu, Ni, Co, Cr, Cd, Sn) QDs was achieved by co-precipitation technique. Zinc acetate ($Zn(CH_3COO)_2.2H_2O$), sodium sulfide (Na_2S) were chosen as source material. Manganese acetate, copper chloride, nickel nitrate, cobalt nitrate, chromium chloride, cadmium acetate and tin chloride are taken as dopant materials for Zn, S, Mn, Cu, Ni, Co, Cr,Cd respectively. The ultra-pure de ionized water was served as solvent for the sample preparation. All the chemicals are analytical grade (AR) with 99.99% purity. To synthesizeZnSnano-powders doped withT, separate solutions were prepared by dissolving 0.98M zinc acetate, 0.02M of Teach and 1M sodium sulfide in 50 ml double distilled water. These solutions were kept under continuous stirring for homogeneity.Solutions were addeddropwise ina beaker. Continuous stirring was carried out at the rate of 1000 rpm for 8 h. Aqueous ammonia solution was added to standardize the pH value of solution at 9.0. After 6 h, a precipitate was received at the bottom of the flask. A wet precipitate was filtered out and washed. The end product was kept in a furnace at 65°C for 8 h. The doping concentration of all the dopant was fixed as 2 %.

Characterization

A powder X-ray diffractometer was used to investigate the crystal structure of $Zn_{0.98}T_{0.02}S$ QDs. The diffracted patterns by RigaKuC/max-2500 diffractometer using CuKa radiation at 40 kV and 30 mA from $2\theta = 0°$ to 70° with scan rate 0.2˚/ min. The structural analysis was carried out using transmission electron microscopy (Philips - CM200) in the range of operating voltage as 20-200kV. The EDX spectra was taken using JEOLJSM 6390.The UV – visible optical absorption and transmittance studies were accomplished using UV – visible spectrometer (Model: lambda 35, Make: Perkin Elmer) from 300 nm to 600 nm at room temperature. Halogen and deuterium lamps were used as sources for visible and UV radiations respectively.

RESULTS AND DISCUSSIONS

X-ray diffraction, TEM, EDX, UV- Visible absorption and transmission studies

XRD patterns of T doped ZnS QDs was shown in figure 1a. All the samples showed cubic structure except Cu doped ZnS structure. All the samples have peaks corresponding to (111), (220) and (311) planes. The 2Ɵ values shifted towards higher angle side confirmed the substitution of T ion in the ZnS host. Due to the ionic size variation Cu addition exhibited mixed state of cubic and hexagonal structure.fig.1b expressed the primary peak intensity of various transition ions doped ZnS QDs. The crystallite size measured using Debye - Scherrer formula and they were ranged from 1.5 nm to 2.5 nm. From the observation, Cr doped ZnS possessed very low particle size [4]. All the 2Ɵ values related to the primary peaks matched with respective JCPDS card number.

TEM picture of Mn doped ZnS QDs and Cr doped QDs were shown in figure 2.a and 2.b as sample. Spherical shaped particles were lucid.Fig.2a and fib 2.b showed the particle agglomeration. Fig 2.c showed the SAED pattern and this result was matched with concern XRD planes value. The EDX Spectra evidenced the doped element presence for Co doping as per the stoichiometric ratio [5].

Fig. 3a explained the absorption behavior of T doped ZnS QDs. Maximum absorption was received for Sn, Cd doping. Cr doping caused highest red shift. Fig. 3b showed the UV- visible transmittance report from 300 nm to 600 nm. From the comparative study a maximum transmittance was occurred for cobalt doping and except Mn doping all the dopant produced red shifts [6]. The band gap values calculated using Tauc's plot and maximum band gap value exhibited for Mn addition and lowest band gap was obtained for Sn and Cd doping. Quantum confinement effect increased the band gap from bulk ZnS since the particle size was reduced. d to d shell electrons shifting played a vital role in the band gap tailoring on ZnS QDs [7].

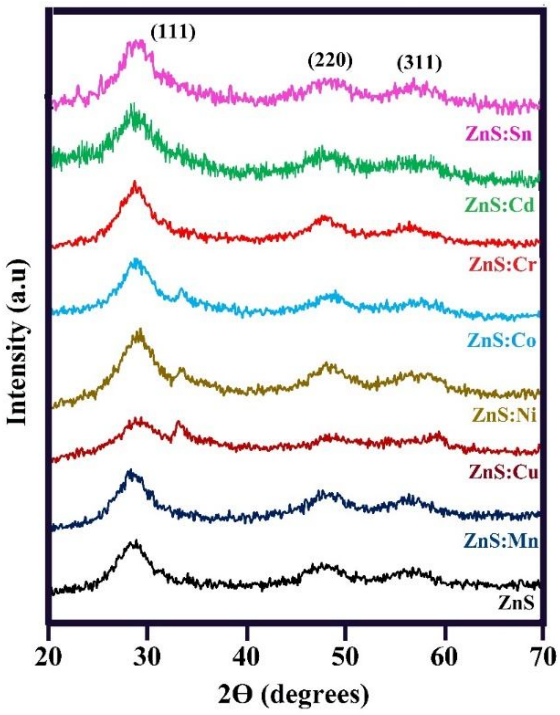

FIGURE 1.a)XRD patterns of ZnS with different elements

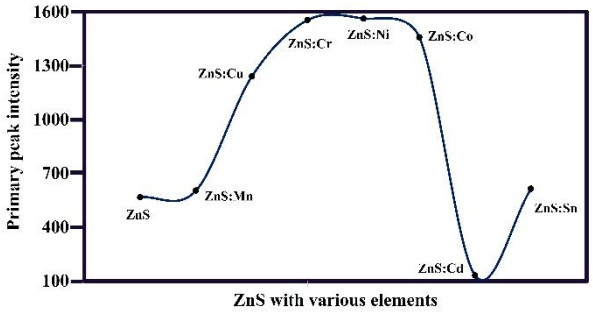

FIGURE 1. b) Peak intensity vs doped elements with ZnS QDs.

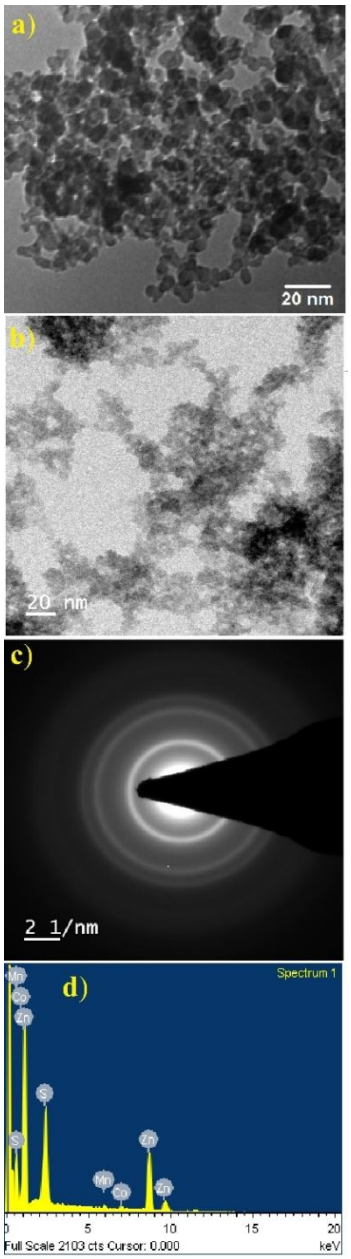

FIGURE 2.a) TEM picture of Mn doped ZnS b) TEM picture of Cr doped ZnS c) SAED patternd) EDX graph for Co doped ZnS.

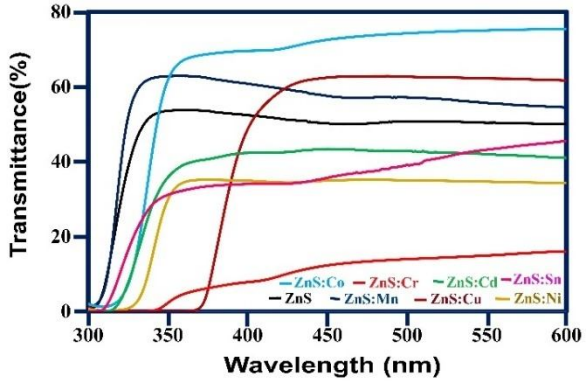

FIGURE 3.a)UV-Transmittance peaks of ZnS with different elements

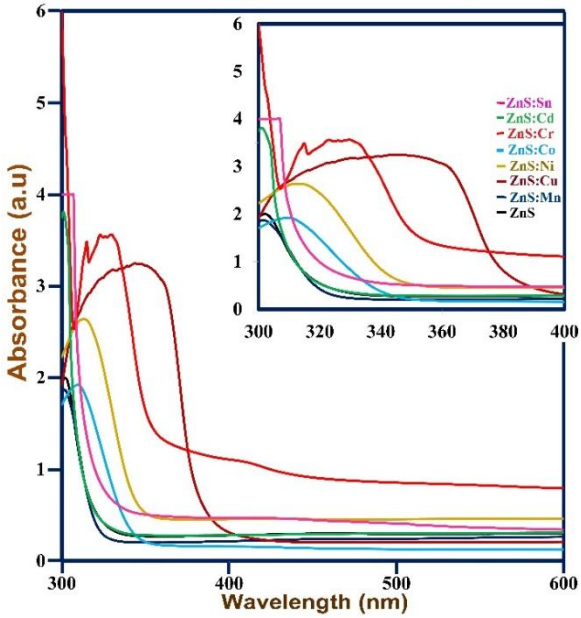

FIGURE 3.a)UV-Transmittance peaks of ZnS with different elements

CONCLUSION

$Zn_{0.98}T_{0.02}S$ (T= Mn, Cr, Cu, Ni, Co, Cd &Sn) QDs have been prepared by co-precipitation method. All the samples exhibited cubic structure without formation of secondary peaks except Cu. Size of the particles measured from XRD results and were within 2 to 3 nm. Cr doped ZnS made more red shift and Sn, Cd had more absorption peak intensity. Co doped ZnSevidenced better transmittance. Optical band gap of doped ZnS materials had a wide range from 3.5 eV to 4.0 eV. In the transition metal group, various ions are doped with ZnS and analyzed their structural and optical properties in order to suggest the materials for optoelectronic device fabrication.

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