Print ISSN: 0974-2115
www.jchps.com Journal of Chemical and Pharmaceutical Sciences

Spectroscopic investigations on Mn^{2+} doped ZnS/CdS nanocomposite powder

J. Madhavi[1], Sk. Johny Basha[1], V. Khidhirbrahmendra[1], L.V. Krishna Rao[2], Ch.Venkata Reddy[3] and R.V.S.S.N. Ravikumar[1]*

[1]Department of Physics, Acharya Nagarjuna University, Guntur-522 510, A.P.
[2]Department of Physics, Sir C.R. Reddy College, Eluru-534 007, A.P.
[3]School of Mechanical Engineering, Yeungnam University, Gyeongsan 712-749, Republic of Korea.
***Corresponding author: E-Mail: rvssn@yahoo.co.in**

ABSTRACT

Chemical precipitation method was used for the synthesis of Mn^{2+} doped ZnS/CdS composite nanopowder at room temperature. The formation of the nano composite structure has been evidenced by XRD and FT-IR. Crystalline nature and size of the particles have been analyzed by X-ray diffraction study with cubic phase of ZnS as well as CdS. The average crystallite size is found to be in the order of nano size and the corresponding lattice parameters, micro strain and dislocation density are evaluated. FT-IR spectrum showed the characteristic vibrational modes related to Zn-S, Cd-S and other functional groups of the present prepared sample.

KEY WORDS: Nanocomposite, Mn^{2+} ions, Semiconductors, X-ray diffraction and FT-IR.

1. INTRODUCTION

The development of new materials, processes and phenomena at nanoscale offers new opportunities in the evolution of nano-systems and nano-structured materials, as well as in their use in multiple applications (Guo and Peng, 2015; Chen, 2014; Huang, 2012; Yang, 2008). Due to requirements like low dimensionality, chemical purity, and chemical and thermal stability in connection with an application domain, a great attention was paid to their design and synthesis (Mandal, 2011; Santra, 2005). In the last decade, composite semiconductor nanomaterials such as core–shell, super-lattices etc., based on cadmium sulphide (CdS) and zinc sulphide (ZnS) with integrated multi functionality of the individual components are increasingly important because of their novel composition of the materials (Sadollahkhani, 2015; Wang, 2010). ZnS and CdS based dilute magnetic semiconductor (DMS) materials have been extensively studied since they are highly multifunctional owing to their contemporaneous structural, magnetic, semiconducting, electromechanical and optical properties (Scholz, 1998; Tripathi, 2008). Mn^{2+} has been the most extensively studied luminescence activator in II–VI semiconductor composite nanopowder (Kulkarni, 2006; Alivisatos, 1996; Norris, 2001; Malik, 2001; Hanif, 2002 and Bao, 2007). Mn^{2+} doped ZnS/CdS composite nanopowder are interesting because of the fact that Mn^{2+} ions provide good traps for the excited electrons, which gives rise to their potential use in nonlinear optics, electronic and optoelectronic devices (Kulkarni, 2006; Lee, 2007; Hullavarad, 2008). These exciting achievements motivated us to investigate Mn^{2+} doped ZnS/CdS composite nanopowder. Mn^{2+} doped ZnS/CdS composite nanopowder has a significant role towards the application in areas such as diluted magnetic semiconductors, light emitting diodes, photoconductors, solar cells, thin film transistors and green lasers as a result of its improved essential properties. In the present paper, Mn^{2+} doped (0.01 mol%) ZnS/CdS composite nanopowder was prepared by chemical precipitation method and characterised with XRD and FT-IR studies.

2. EXPERIMENTAL

Materials: All the chemical reagents used were analytical grade without further purification. All the chemical reagents were purchased from Merck chemicals, Mumbai, India. Zinc acetate Zn $(CH_3COO)_2.2H_2O$ Cadmium acetate, $(Cd(CH_3COO)_2.2H_2O)$ sodium sulphide (Na_2S), manganese oxide (MnO) and ethanol (C_2H_6O) were used as precursors. Deionized water was used for all dilution and sample preparation. All the chemicals are above 99% purity. All the glassware used in this experimental work was acid washed.

Synthesis of Mn^{2+} doped ZnS/CdS composite nanopowder: Two-step chemical precipitation method has been used to synthesize Mn^{2+} doped ZnS/CdS composite nanopowders.

First step: Appropriate concentrations of zinc acetate was dissolved in deionised water and stirred for 10 min at room temperature. Then 50 ml of deionised water-ethanol matrix and an equal molar amount of Na_2S in another deionised water–ethanol matrix were mixed drop by drop. The mixture was stirred magnetically at 80°C and kept for 8 h, until a homogeneous white solution was obtained. The contents were centrifuged at 10,000 rpm about 30 min, several times washed with water and ethanol to eliminate impurities and dried at 80°C for 1h. For the better yield of ZnS nanopowders temperature rises to 120°C and kept for 2 h in hot air oven. A powder with white colour was obtained which confirmed ZnS**.**

Second step: Powder cadmium acetate was dispersed in 50 ml of deionised water and allowed to stir for 10 min. Then 50 ml of deionised water-ethanol matrix and an equal molar amount of Na_2S is added to the solution in the above manner. Now CdS is precipitated at the bottom of the solution. Then homogeneous solution of ZnS is added

to the CdS. Now the white solution turned to light yellow colour, the indication of formation of CdS particles on ZnS. Finally, 0.01 mol% MnO is added to the above solution and left for 3 h. The precipitates were centrifuged, washed with water, ethanol and dried at 80°C. The yield of the Mn^{2+} doped ZnS/CdS nanocomposite was obtained. The synthesized Mn^{2+} doped ZnS/CdS composite nanopowder was characterised using different techniques.

Characterization techniques: Powder X-ray diffraction pattern was recorded on Shimadzu 6100 X-ray diffractometer with CuKα radiation (1.5406Å). Fourier Transform Infrared (FT-IR) spectrum was recorded using KBr pellet on Shimadzu IRAffinity-1S in the range of 4000–400 cm^{-1}.

3. RESULTS AND DISCUSSION

X-ray diffraction analysis: The X-ray diffraction pattern of Mn^{2+} doped ZnS/CdS composite nanopowder is shown in Fig.1. The sharp peaks in XRD pattern may be originated from well-ordered crystals. All the diffraction peaks marked in circles are indexed to a cubic structure of ZnS (JCPDS: 05-0566) with lattice cell parameters a = 0.3254 and c = 0.5210 nm. The peaks marked in triangles are indexed to cubic structure of CdS (JCPDS: 80-0019) with lattice cell parameters a = 0.5627 nm. The diffraction peaks observed at 2θ = 27.66, 34.54 and 56.76 are assigned to the diffraction planes (1 1 1), (2 0 0), (3 1 1) of cubic structured ZnS. The peaks observed at 2θ = 26.33, 31.80, 45.84, and 54.27 are corresponding to planes (1 1 1), (2 0 0), (2 2 0) and (3 1 1) of cubic phase of CdS. No additional peaks corresponding to the impurity phase were observed which reveals that the impurity ions does not change crystal structure and sample is in good purity and well crystallinity. This result confirms successful synthesis of ZnS-CdS composite nanopowder. Shifting in peak positions is due to presence of micro strain in the lattice. The average crystallite size of Mn^{2+}doped ZnS/CdS composite nanopowder is calculated using Debye-Scherrer's formula (Cullity, 2001).

$$D = 0.9\,\lambda/\beta\cos\theta$$

Where D is the average crystallite size, λ is incident wavelength (Cu Kα), β is full width at half maximum (FWHM) and θ is diffraction angle. The average crystallite size was estimated from most intense diffraction peak as 14.85 nm. The micro strain (ε) was calculated using the expression (Aswani, 2014),

$$\varepsilon = \beta\cos\theta\,/4.$$

Generally, crystallite size (D) decreases with increase of micro strain and vice-versa. Similar trend is observed in the present study. The evaluated micro strain (1.975×10^{-3}) is to be calculated and dislocation density = $1/D^2$ is $4.53x10^{15}$ lines/m^2. Scherrer's formula gives information about the average size of crystallite but it neglects the effect of strain in the crystal.

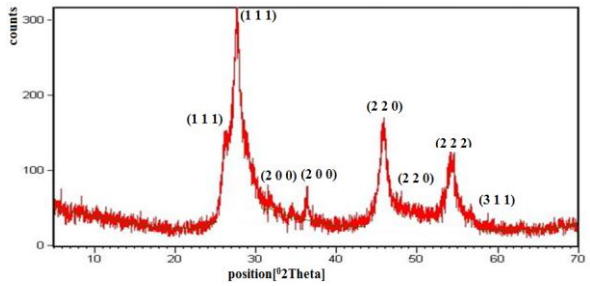

Fig.1. X-ray diffraction pattern of Mn2+ doped ZnS-CdS composite nanopowder

FT-IR analysis: Fig.2, shows FT-IR spectrum of Mn^{2+}doped ZnS/CdS composite nanopowder, which exhibits the characteristic bands of ZnS and CdS. In addition to this, the spectrum exhibits fundamental vibrations O–H groups. The band observed at 419 cm^{-1} is corresponds to metal sulphide bond (Cd-S), we further performed the formation of CdS (Nikita, 2015). The band appeared at 612 cm^{-1} is attributed to the stretching vibrational mode of Zn-S (Kuppayee, 2012). The band observed at 1116 cm^{-1} is assigned to O-H stretching mode of H_2O molecule. The band at 1539 cm^{-1} corresponds to the C= O stretching vibration (Thirumala Rao, 2015). The vibrational band observed at 1631 cm^{-1} is a characteristic of symmetric bending vibration of H_2O molecule. A broad peak in the range of 3200–3500 cm^{-1} corresponds to the vibrational mode of O–H bond (Nakamoto, 1997).

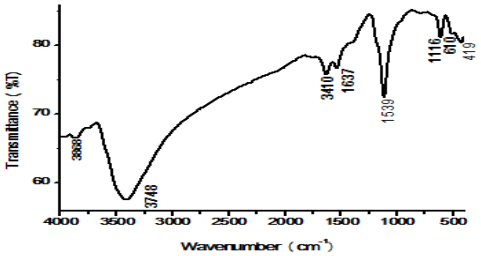

Fig.2. FT-IR spectrum of Mn2+doped ZnS/CdS composite nanopowder

4. CONCLUSION

In summary, Mn^{2+} doped ZnS/CdS composite nanopowder was synthesized by chemical precipitation method at room temperature and are characterised by spectroscopic techniques XRD and FT-IR. XRD pattern indicate the structure of the crystal is cubic. FT-IR spectrum show characteristic vibrations of ZnS, CdS and other functional modes of vibrations.

5. ACKNOWLEDGEMENTS

J. Madhavi is thankful to Acharya Nagarjuna University for providing University Research Fellowship for providing financial assistance to carry out the present research work. Authors are also thankful toUGC-DSA1, DST-FIST for providing financial assistance to the department of Physics, Acharya Nagarjuna University, Guntur, India.

REFERENCES

Alivisatos AP, Semiconductor clusters, Nanocrystals and Quantum Dots, Science, New series, 271, 1996, 933-937.

Aswani T, Babu B, Pushpa Manjari V, Joyce Stella R, Thirumala Rao G, Rama Krishna CH, Ravikumar RVSSN, Synthesis and spectral characterisations of trivalent ions doped CdO nanopowders, Spectrochimic Acta part A, 121, 2014, 544–550.

Bao N, Shen L, Takata T, Domen K, Gupta A, Yanagisawa K, Grimes CA, The formation of a p–*n* junction in Cu3P/CdS NRs leads to fast charge transfer and enhanced photo catalytic activity under visible light irradiation, Journal of Physical Chemistry, 111, 2007, 17527-17534.

Cullity BD, Stock SR, Elements of X-ray Diffraction, 3, Prentice Hall, New Jersey, 2001, 400.

Guo J, Peng C, Synthesis of ZnO nanoparticles with a novel combustion method and their C_2H_5OH gas sensing properties, Ceramic International, 41, 2015, 2180–2186.

Hani KM, Meulenberg RW, StrouseAm GF, Magnetic ordering in doped Cd(1-x)Co(x)Se diluted magnetic quantum dots, Journal of Chemical Society, 124, 2002, 11495-11502.

Hullavarad NV, Hullavarad SSK, Arulkar PC, Cadmium sulphide (CdS) nanotechnology: synthesis and applications, Journal of Nanoscience and Nanotechnology, 8, 2008, 3272-3799.

Kulkarni SS, Kazakova O, Holmes JD, Dilute magnetic Semiconductor nano wires, Journal of Applied Physics A-Materials & Processing, 85, 2006, 277-286.

Kuppayee M, Vanathi Nachiyar GK, Ramasamy V, Enhanced photoluminescence properties of ZnS: $Cu_2þ$ nanoparticles using PMMA and CTAB surfactants, Material Science and Semiconducting Processing, 15, 2012, 136–144.

Lee JC, Subramanian NC, Lee JW, Kang TW, Ferroelectric behavior and reproducible Bi-stable resistance switching property in K-doped ZnO thin films as candidate for application in non-volatile memories, Applied Physics Letters, 90, 2007, 262909-262912.

Malik MZ, Brien PO, Revaprasadu NJ, Characterisation of Mn Doped CdS Nano particles, Journal of Material Chemistry, 11, 2001, 2382-2386.

Mandal P, Singh A, Kasture S, Gopal AV, Vengurlekar AS, Plasmon assisted intense blue–green emission from ZnO/ZnS nano-crystallites, Optical Materials, 33, 2011, 1786–1791.

Nakamoto K, Infrared Raman Spectra of Inorganic and Coordination Compounds, Part-A and B, John Wiley and Sons, New York, 1997.

Nikita Patel H, Thesis Synthesis of Undoped and Mn/Ni/Co Doped, CdS Nanoparticles by chemical route, Sardar Patel University, 2015, 102-119.

Norris DJ, Yao N, Charnock FT, Kennedy TA, High-Quality Manganese-Doped ZnSe Nanocrystals, Nano Letter, 1, 2001, 3-7.

Sadollahkhani A, Nur O, Willander M, Kazeminezhad I, Khranovskyy V, Eriksson MO, Yakimova R, Holtz POA detailed optical investigation of ZnO@ZnS coreshell nanoparticles and their photo catalytic activity at different pH values, Ceramic International, 41, 2015, 7174–7184.

Scholz SM, Vacassy R, Dutta J, Hoffmann HJ, Mie Scattering effects from mono dispesed ZnS nano sphere, Journal of Applied Physics, 83, 1998, 7860-7866.

Thirumala Rao G, Babu B, Joyce Stella R, Pushpa Manjari V, Venkata Reddy Ch, Shim J, Ravikumar RVSSN, Synthesis and characterisation of VO^{2+} doped ZnO-CdS composite nano powder, Journal of Molecular Structure, 1081, 2015, 254–259.

Tripathi B, Singh F, Avasthi DK, Bhati AK, Das D, Vijay YK, Investigation on microstructures and interface character of B4C particles reinforced, Journal of Alloys and Compounds, 454, 2008, 97-101.