



An Extrapolation of Manganese Mn Incapacitated Copper Sulphide (CuS) Nano Particles by Hydrothermal Method

^aL.Thilagavathi, ^aDr.M.Venkatachalam, ^aDr.M.Saroja, ^bDr.T.S.Senthil

*^aDepartment of Electronics, Erode Arts and Science College, Erode, India ^bDepartment of
Physics, Erode Sengunthar Engineering College, Perundurai, India ^althilagakavi@gmail.com*

Abstract

Manganese (Mn) doped CuS nano particles were synthesized from copper (II) chloride, manganese (II) chloride, and thiourea by hydro thermal method. Incapacitating of Mn ions along with CuS nano particles existence were identified using the energy dispersive analysis of X-rays (EDAX). The X-ray diffraction (XRD) exposed the nanoparticles has hexagonal structure. The scanning electron microscopy (SEM) shown that the Mn doped CuS nanoparticles having spherical like morphology. The transmission electron microscopy (TEM) images exhibited that the particles size varies from 18 to 28 nm. The optical absorption spectra showed direct band gap values of 1.8 and 1.9 eV. The obtained results are explained in details.

Keywords: *Copper sulphide, Manganese, Nano particles, Optical absorption, Morphology*

Introduction

Semiconductor nano materials have revealed special electrical, optical, thermal, magnetic properties compared from those of their bulk materials, prominent to their use in advanced technology (1–4). The properties of the nano materials are significantly identified their morphology. Thus there has been growing interest in the well-ordered synthesis of nanostructures having different morphologies for their different prospective applications in photonic, as catalyst, drug delivery, and solar cell and solar radiation absorber (5, 6). In nano scale, the compound semiconductors appropriate to transition metal chalcogenides (TMC) shows unexpected physical and chemical properties are subject to the morphology of the nano materials (7,8).

Covellite is a rare copper sulfide (CuS) mineral. Also it is one of the member of the TMC compound semiconductor materials. It has wide applications in solar control coating, (9) dyesensitized solar cell, (10) lithium ion batteries, (11) gas sensor, (12) catalysis (13, 14) and photo catalyst, (15, 16) photo degradation (17). The synthesis by various methods (18-25) and with different Cu_xS compounds, such as Cu_2S , $Cu_{1.96}S$, $Cu_{1.75}S$ and CuS with various morphologies such as nanoparticles, (21-24) nano rods, (26) nanowires, (7) nano platelets, (18) nano flowers, (15) nano whiskers, (25) nanocrystals, (23) nano ribbons (27) and nanotubes (20) have concerned reputation due to their owing properties and potential applications in numerous fields. Literature survey exposes that properties and characteristics of CuS recovers and changes by doping with different elements such as Zn, (28) Fe, (29) and Ni, (30) and (Mn) doped CuS nanoparticles.

Here the authors show the synthesis of Mn doped CuS nanoparticles by hydro thermal method with different temperature. The study of Mn doped CuS nanoparticles were done by structural, morphological, and optical analysis. The obtained results are deliberated in details.

Preparation method

In typical synthesis of CuS nano particles, copper (II) chloride, thiourea are dissolved in water separately with constant stirring. All the dissolved precursor solutions are mixed drop wise with sodium alginate colloidal solution and then it is permitted to vigorous stirring up to 1 h for improve the chemical reaction. During this, the reaction solution colour is changed from white colour to dark blue colour. It is clearly showed that the formation of CuS nano particles. The reaction solution is permitted to heat using microwave treatment for 10 min. Then, the precipitate of final solution is washed with DI water in several times. It is also followed by washing with ethanol for four times and it is dried in oven at 150 °C. The dried products of CuS nano particles are prepared.

The Mn doped CuS was prepared using doctor blade method. The paste was produced by mixing of 0.5 gram of CuS powder with a mixture solution (0.5 gram

Manganese nitrate, 6 gram of α -terpineol, 1 gram of cellulose, and 25 ml of ethanol, which was solicited for 18 h at $1,500 \text{ Wcm}^{-2}$). This paste were used as coating materials on a FTO conducting glass plate (Hartford FTO, approximately $30\Omega \text{ cm}^{-2}$, 80 % transmittance in visible region) using the doctor blade technique. The Mn doped CuS nano particles are collected from the glass plate. The prepared nano particles were annealed at different temperatures like 100°C, 150°C and 200°C for 90 mins.

Result and Discussion

X-ray diffraction

X-ray diffraction pattern of the synthesized Mn doped CuS nanoparticles at different temperatures are shown in Figure. 1.

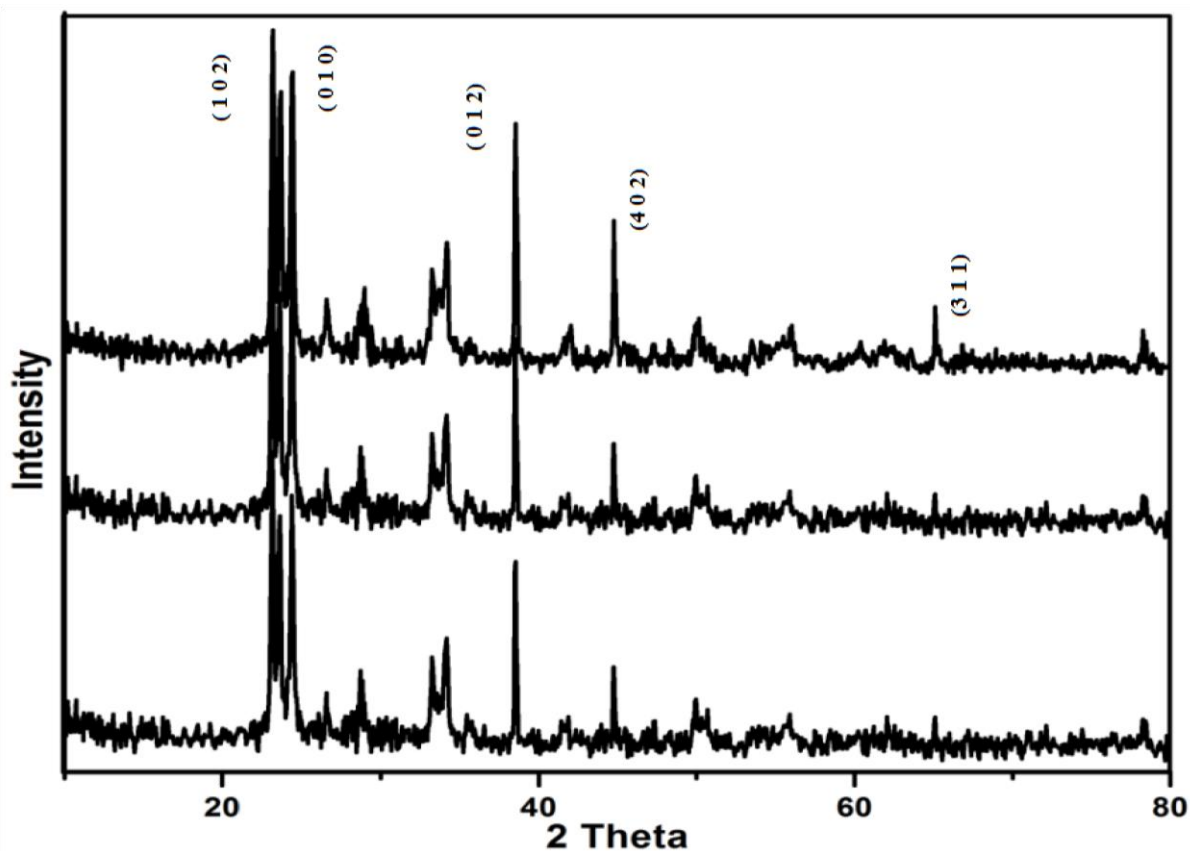


Figure - XRD Patterns of Mn doped CuS nanoparticles at different temperatures Figure shows the X-ray diffraction patterns of Mn doped CuS nanoparticles in different temperatures. The diffraction peaks are located at angles (2θ) of 17.98, 24.53, 28.44, 31.43 and 32.15 which correspond to the (102), (010), (012), (402) and (311) planes of CuS and indicates that the nano particle are of hexagonal phase (JCPDS No. 05-0394). The observed diffraction pattern of the Mn doped CuS nanoparticles states that there is no additional phase of manganese or manganese oxide, since Mn has been incorporated into the lattice of CuS. For the Mn doped CuS nanoparticles, the strength of peaks of all the crystal planes clearly increased with the increase of temperature, due to the reformation of the CuS structure. The diffraction pattern also shows that the peaks have been lifted to higher 2θ values. This shift in the peaks of Mn doped CuS nanoparticles might be due to the substitution of Mn for Cu in the lattice.

Morphological analysis of Mn doped CuS nanoparticles

The surface morphology of Mn doped CuS nanoparticles is evident from SEM images and is shown in figure. From SEM images it is observed that the nanoparticles are like spherical in shape.

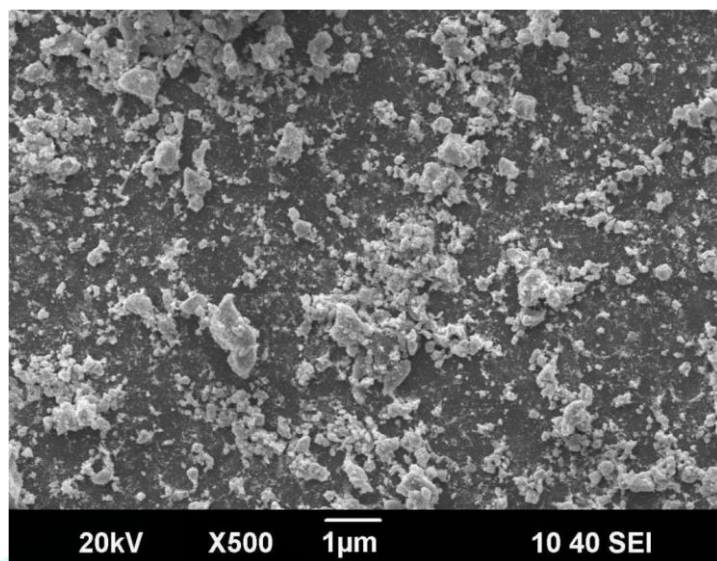


Figure - SEM and EDX images of Mn doped CuS nanoparticles

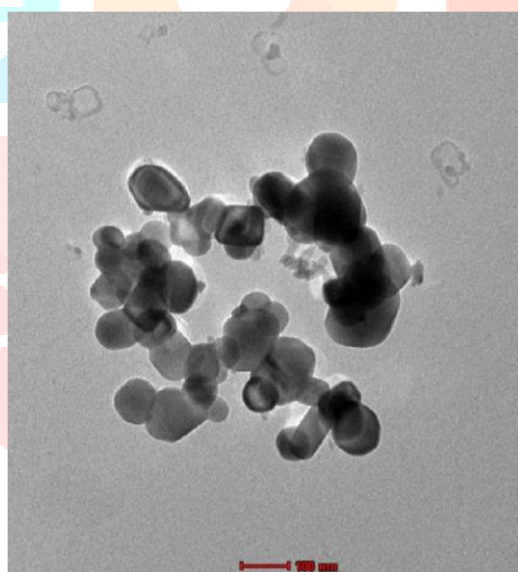


Figure - TEM and EDX images of Mn doped CuS nanoparticles

Figure shows the scanning electron microscope and transmission electron microscope images of Mn doped CuS nano particles. The image shows spherical like uneven distribution of crystals. The diameter of the Mn doped CuS nano particles were observed to increase with increasing temperature. Therefore it can be assumed that there is some correlation between the structural morphology of the Mn doped CuS nano particles and the annealing temperature. The transmission electron microscopy (TEM) images exhibited that the particles size varies from 18 to 28 nm.

UV-VIS NIR Spectral Analysis of Mn doped CuS nanoparticles

The optical absorption properties of the Mn doped nano particles are analysed from UV-visible spectroscopy and the results are presented in Fig. 3.

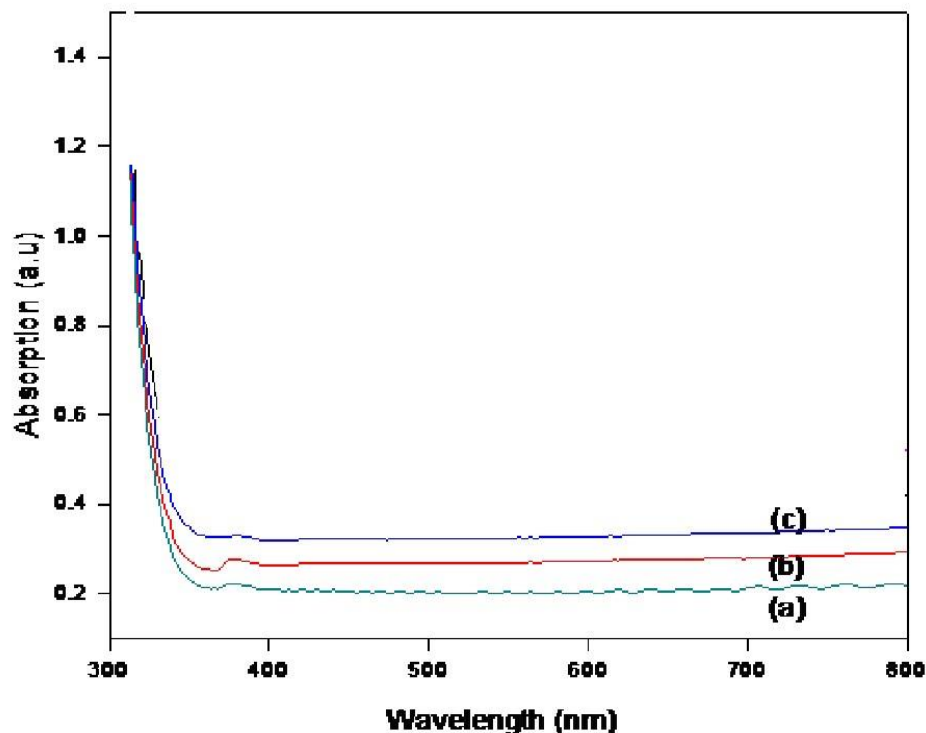


Figure - UV-VIS spectral analysis of Mn doped CuS nanoparticles at different temperatures

Though this small change of the crystallite size is revealed on the UV– visible spectral data in the region of 382–396 nm wavelengths with a red shift of absorption wavelength. It is found to be around 1.8 eV for 100°C and 150°C and 200°C WO₃ nanoparticles are found to be 1.85 eV and 1.9 eV which is higher than the band gap of 100°C Mn doped CuS nanoparticles. The growth in the band gap may be due to the rise in the temperature. The optical absorption co-efficient is related to the calculated energy band gap 1.85 eV is in good agreement with previous researches.

FTIR Analysis of Mn doped CuS nanoparticles

Fourier transform infrared analysis is an expectant method for observing molecular vibrations. Figure 4 shows the FTIR spectra of Mn doped CuS nano particles. FTIR spectra exists the indication to observe in plane and out of plane segmental vibration of atoms and molecules with correlated energies in the IR region. The stretching, bending and bonding can be renowned through FTIR analysis. In CuS, the atoms of Cu are situated at the centre of the hexagonal and sulphide atoms are at the vertices, thus forming a Cu-S-Cu. In our work, Cu-S and Cu-S-Cu ultimate vibrations are found.

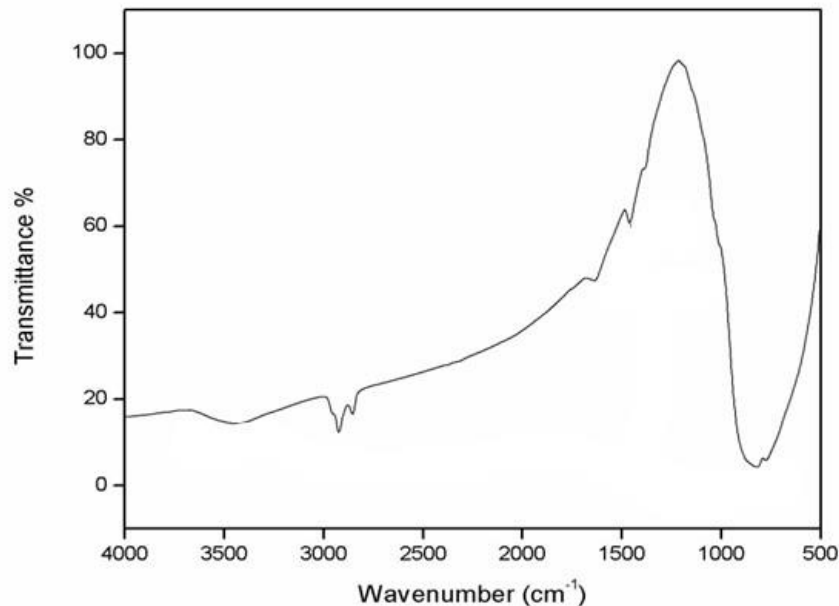


Figure - FTIR analysis of Ni doped CuS nanoparticles

The symmetric stretching vibration (ν_{sym}) connected to CuS and correlated molecules (Cu–OH...H₂O) is measured as a significant peak with a broad band at 3542 cm⁻¹. Stretching vibration of O–H group is noticed at 2822 cm⁻¹ and bending vibration is at 1518 cm⁻¹. Also the ratification for the formation of OH group in the spectra is observed at 1515 cm⁻¹. When the samples are annealed asymmetric vibrations are noticed due to the presence of mixed phases. The results in this study are in good agreement with previous researches [14].

Conclusion

Mn doped CuS nano elements were fused by hydro thermal process. Incapacitating of Mn ions along with CuS nano particles existence were identified using the energy dispersive analysis of X-rays (EDAX). The X-ray diffraction (XRD) uncovered the nanoparticles has hexagonal arrangement. The scanning electron microscopy (SEM) revealed that the Mn drugged CuS nanoparticles having spherical like morphology. The transmission electron microscopy (TEM) images unveiled that the particles magnitude varies from 18 to 28 nm.

The optical absorption spectra showed direct band gap values of 1.8 and 1.9 eV.

References

1. J. Qian, K. Wang, Q. Guan, H. Li, H. Xu, Q. Liu, W. Liu, and B. Qiu, *Appl. Surf. Science.* 228, 633 (2014).
2. W. U. Huynh, J. J. Dittmer, and A. P. Alivisatos, *Science* 295, 242 (2002). 3. H. H. Kung and M. C. Kung, *Catal. Today* 97, 219 (2004).
4. Y. J. Yang, J. Zi, and W. Li, *Electrochim. Acta* 114, 126 (2014).
5. S. H. Jiao, K. Jiang, Y. H. Zhang, M. Xiao, L. F. Xu, and D. S. Xu, *J. Phys. Chem. C* 112, 3359 (2008).
6. Y. D. Zhu, J. Peng, L. P. Jiang, and J. J. Zhu, *Analyst* 139, 649 (2014).
7. F. Zhang and S. S. Wong, *Chem. Materials.* 21, 4541 (2009).
8. Z. Wang, L. L. Daemen, Y. Zhao, C. S. Zha, R. T. Downs, X. Wang, Z. L. Wang, and R. J. Hemley, *Nat. Materials.* 4, 922 (2005).
9. A. Bollero, S. Fernandez, K. Z. Rozman, Z. Samardzija, and M. Grossberg, *Thin Solid Films* 520, 4184 (2012).
10. K. D. Yuan, J. J. Wu, M. L. Lui, L. L. Zhang, F. F. Xu, L. D. Chen, and F. Q. Huang, *Appl. Phys. Letters.* 93, 132106 (2008).
11. Y. Chen, C. Davoisne, J. M. Tarascon, and C. Guery, *J. Mater. Chem.* 22, 5295(2012).
12. A. A. Sagade and R. Sharma, *Sensors. Actuators, B* 133, 135 (2008).
13. S. Y. Kuchmii, A. V. Korzhak, A. E. Raevskaya, and A. I. Kryukov, *Theor. Exp. Chem.* 37, 31 (2001).
14. A. E. Raevskaya, A. L. Stroyuk, S. Y. Kuchmii, and A. I. Kryukov, *J. Mol. Catal. A: Chem.* 212, 259 (2004).
15. Z. Cheng, S. Wang, Q. Wang, and B. Geng, *Cryst. Eng. Comm.* 12, 144 (2010).
16. M. Luo, Y. Liu, J. Hu, J. Li, J. Liu, and R. M. Richards, *Appl. Catal., B* 125, 180 (2012).
17. X. Wang, Z. Fang, and X. Lin, *J. Nanoparticles. Res.* 11, 731 (2009).
18. J. Zhang and Z. Zhang, *Mater. Letters.* 62, 2279 (2008).
19. J. Liu and D. Xue, *J. Cryst. Growth* 311, 500 (2009).
20. T. Thongtem, A. Phuruangrat, and S. Thongtem, *Mater. Letters.* 64, 136 (2010).
21. H. Wang, J. R. Zhang, X. N. Zhao, S. Xu, and J. J. Zhu, *Mater. Letters.* 55, 253 (2002).
22. Y. J. Yang and S. Hu, *J. Solid State Electrochem.* 12, 1405 (2008).
23. L. Gao, E. Wang, S. Lian, Z. Kang, Y. Lan, and D. Wu, *Solid State Commun.* 130, 309 (2004).
24. J. Xu, X. Cui, J. Zhang, H. Liang, H. Wang, and J. Li, *Bull. Materials. Sci.* 31, 189 (2008).
25. S. H. Chaki, M. P. Deshpande, K. S. Mahato, M. D. Chaudhary, and J. P. Tailor, *Adv. Sci. Letters.* 17, 162 (2012).
26. K. V. Singh, A. A. M. Morales, G. T. S. Andavan, K. N. Bozhilov, and M. Ozkan, *Chem. Materials.* 19, 2446 (2007).
27. C. Tan, R. Lu, P. Xue, C. Bao, and Y. Zhao, *Mater. Chem. Physics.* 112, 500 (2008).

28. M. A. Yildirim, A. Ates, and A. Astam, *Physica E* 41, 1365 (2009).
29. L. Z. Pei, J. F. Wang, X. X. Tao, S. B. Wang, Y. P. Dong, C. G. Fan, and Q. F. Zhang, *Materilas. Charact.* 62, 354 (2011).
30. Z. H. Wang, D. Y. Geng, Y. J. Zhang, and Z. D. Zhang, *Mater. Chem. Physics.* 122, 241 (2010).

