

Synthesis and Properties of (Mn, Ni) co-doped ZnS nanoparticles

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DOI: 10.5185/amp.2018/1417

www.vbripress.com/amp

Abstract

Pure and (Mn, Ni) co-doped ZnS nano particles are synthesized by co-precipitation method using Poly Vinyl Pyrrolidone (PVP) as stabilizer. Powder XRD results exhibit cubic blended structure for all samples. The average crystallite sizes observed to be between around 2-3 nm. Uneven changes of crystal structure of concerned nanoparticles are confirmed by the Transmission Electron Microscopy (TEM) studies. The crystalline sizes obtained from TEM (3-5 nm) agree well those of XRD data. The SEM micro graphs of (Mn, Ni) co-doped nanoparticles result in agglomeration with spherical shape. The EDAX Spectra reveal that in the chemical composition of the prepared samples, the co-doped elements are incorporated into ZnS lattice. Photoluminescence (PL) has been studied at 306 nm wavelength. Pure sample exhibits sharp peaks at 438 nm, 450 nm and 466 nm. The (Mn, Ni) co-doped powders exhibit slightly less intense peaks. The magnetic measurements reveal that the co-doped nanoparticles exhibit Room Temperature Ferromagnetism (RTFM). Copyright © 2018 VBRI Press.

Keywords: ZnS nanoparticles, XRD, PL, SEM with EDAX, TEM, HR-TEM and VSM.

Introduction

Semiconducting particles at nanolevel exhibit specific chemical, magnetic, optical and electrical properties [1]. Nanoparticles exhibit surface reactivity due to their large surface area to volume ratio [2, 3]. Capping agents reduces the same, and co-precipitation is also one of the methods used to obtain nanoparticles at nanorange [4-9]. ZnS is an important material with wide band gap (3.67eV) in compound semiconductors used in flat panel displays, optical coatings, electro luminescent devices, and photo conductors [10-12]. Dopant impurity can show different luminescent properties in doped materials and cause the change in the electronic structure and transition probabilities of host material. PL properties are observed in ZnS nanopowders by doping various transition and rare earth elements [13-17]. In doped ZnS nanopowders, doped material ions settled in ZnS lattice sites and behave as a trap site for holes and electrons. The excitation of electron takes place from ZnS valence band to conduction band by emitting (or) absorbing energy is equal to the energy gap between valence band and conduction band. Two various kinds of ions present in ZnS materials exhibits fluorescence, which is different from emission due to single ion and is very useful for white light generation [18-20].

This paper deals with preparation of Mn^{2+} , Ni^{2+} in doped ZnS nanoparticles at laboratory temperature with the technique of co-precipitation with PVP stabilizer. The composition, structure and shape of powders are studied using EDAX, XRD, SEM, TEM,

Photoluminescence (PL) and Vibrating Sample Magnetometer (VSM) respectively. Mn ion is responsible for brilliant photoluminescence in co-doped (Mn, Ni).

Synthesis and characterizations

Undoped and doped ZnS nanoparticles have been synthesized by using co-precipitation method. Zinc Acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$], Na_2S , Nickel Chloride [$NiCl_2 \cdot 6H_2O$] and Manganese Acetate tetra hydrate [$Mn(CH_3COO)_2 \cdot 4H_2O$] are used for preparation of $Zn_{1-(x+y)}Mn_xNi_yS$ ($x = 1, 3, 5$ mol% at $y = 3$ mol% constant) composition, Zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$] is dissolved in double distilled water, then Sodium sulfide solution is added drop-by-drop with constant magnetic stirring. A white precipitate is formed. After this [$Mn(CH_3COO)_2 \cdot 4H_2O$], $NiCl_2 \cdot 6H_2O$ powders are added to the above white precipitate under continuous magnetic stirring. Thus (Mn, Ni) co-doped ZnS precipitate is formed. To stabilize the nanopowders, PVP solution is added to the above precipitate for stabilization. The stabilized precipitate is washed many times with double distilled water. This precipitate is dried at temperature of 80°C for 8 hours. This dried sample is used for further investigations.

The following instruments are used to characterize the ZnS nanoparticles and their doping combinations. XRD pattern is recorded with operating wavelength $\lambda = 0.153906$ nm. Photoluminescence (PL) studies

are investigated with EDINBURGH UV-VIS-NIR (FLS-980) spectrometer using Xenon arc lamp (450 W). The morphological shape, elemental analysis, and size of dopants are investigated by SEM, EDAX, TEM, SAED and HR-TEM. Magnetic properties are investigated with VSM magnetometer at 17×10^3 gauss.

Results and discussions

X-Ray diffraction studies

This technique is used to study the influence of the structure of (Mn, Ni) co-doped nanoparticles. Figure shows XRD peaks of pure and co-doped ZnS nanoparticles. From Fig. 1. It has been observed that there are three most preferred planes of orientation namely (1 1 1), (2 2 0) and (3 1 1), at 2θ values 28.88° , 48.22° and 57.66° , all the peaks are attributed to FCC structure of ZnS. The observed XRD peaks match with the standard data. Shapes of the peaks indicate nanocrystallites of the sample without any Mn and Ni presence. These results agree well with previous investigations [21, 22]. The average nanocrystallite size is evaluated by using Debye–Scherrer’s formula [23],

$$D = \frac{0.91 \lambda}{\beta \cos \theta}$$

XRD studies yield average sizes (2-3 nm) as given in Table 1.

Table 1. Structural Calculations of Pure and (Mn, Ni) co-doped ZnS nanoparticles.

Sample	2 θ (Deg.)	Plane (hkl)	Inter planer spacing d(Å)	Lattice constant a(Å)	FWHM (rad)	Average Crystalline Size D (nm)
Pure ZnS	28.98	(111)	3.07741	5.3489	0.06511	2.380
	48.38	(220)	1.87913		0.07298	
	56.43	(311)	1.62866		0.05500	
ZnS: (1% Mn, 3% Ni)	28.87	(111)	3.0888	5.3534	0.06720	2.451
	48.24	(220)	1.8842		0.07568	
	56.66	(311)	1.6225		0.04887	
ZnS: (3% Mn, 3% Ni)	28.66	(111)	3.1110	5.3664	0.06737	2.420
	48.24	(220)	1.88425		0.07121	
	56.66	(311)	1.6225		0.05236	
ZnS: (5% Mn, 3% Ni)	28.87	(111)	3.0888	5.3536	0.06755	2.657
	48.24	(220)	1.8842		0.07942	
	56.66	(311)	1.6225		0.043411	

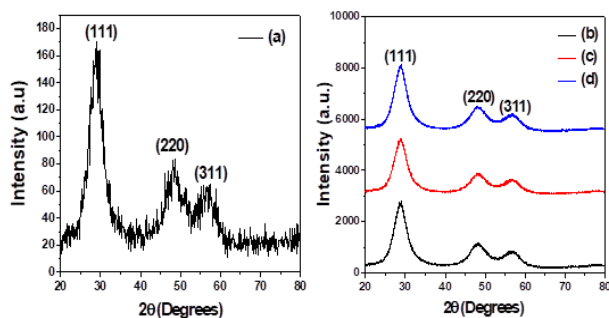


Fig. 1. XRD Spectra of (a) un-doped ZnS, and (b) 1 mol % doped Mn, (c) 3 mol % doped Mn, (d) 5 mol % doped Mn with 3 mol % of Ni into ZnS nanoparticles.

Morphological studies (SEM and EDAX)

The morphological structure of (Mn, Ni) co-doped ZnS nanoparticles are studied by SEM and the micrographs of SEM are shown in Fig. 2. The elemental analyses of the samples are analyzed by EDAX spectra. The compositional values are reported in Table 2.

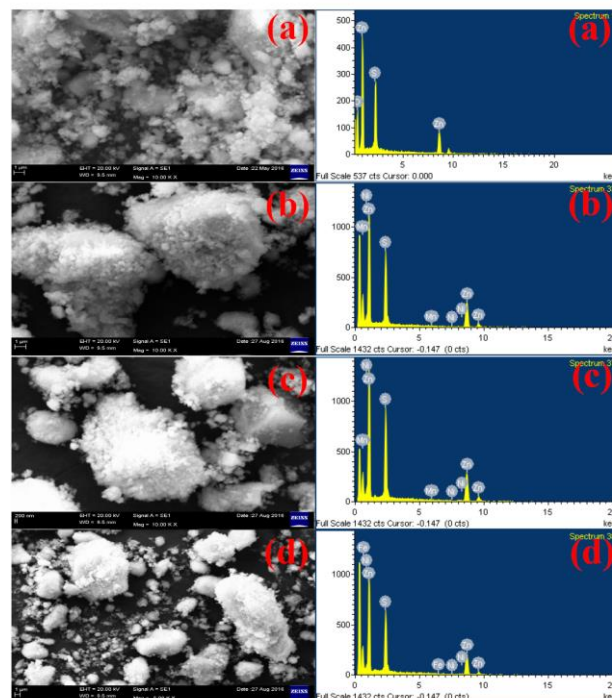


Fig. 2. SEM and EDAX images of (a) un-doped ZnS and (b) 1 mol % doped Mn, (c) 3 mol % doped Mn, (d) 5 mol % doped Mn with 3 mol % of Ni into ZnS nanoparticles.

Table 2. Elemental analysis of pure and (Mn, Ni) co-doped ZnS nanoparticles.

Element	Zn		S		Mn		Ni	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
Pure ZnS	58.28	20.19	41.72	79.81	0.00	0.00	0.00	0.00
1 mol % Mn and 3 mol % Ni	65.51	49.45	31.14	47.93	3.12	2.42	0.24	0.20
3 mol % Mn and 3 mol % Ni	59.60	44.66	31.96	48.83	8.37	6.45	0.07	0.06
5 mol % Mn and 3 mol % Ni	55.19	40.85	33.42	50.44	10.90	8.30	0.50	0.41

SEM images indicate that particle agglomeration decreases with PVP capping agent, and the particles are homogeneously distributed and nearly spherical in shape as shown in Fig. 3. The evaluated values from TEM images (3 to 4 nm) agree well with the XRD calculations.

TEM, HRTEM and SAED analysis

The TEM analysis results intune with size and surface morphology. The typical TEM micrographs of $Zn_{1-(x+y)}$

Mn_xNi_yS ($x=1, 3, 5$ mol % at $y=3$ mol % constant) are shown in **Fig. 3**. In the samples studied, the grains are spherical and isolated. From the SAED pattern, it is noticed that ZnS:(Mn, Ni) co-doped all samples have zinc blended structure with miller indices (111), (220) and (311).

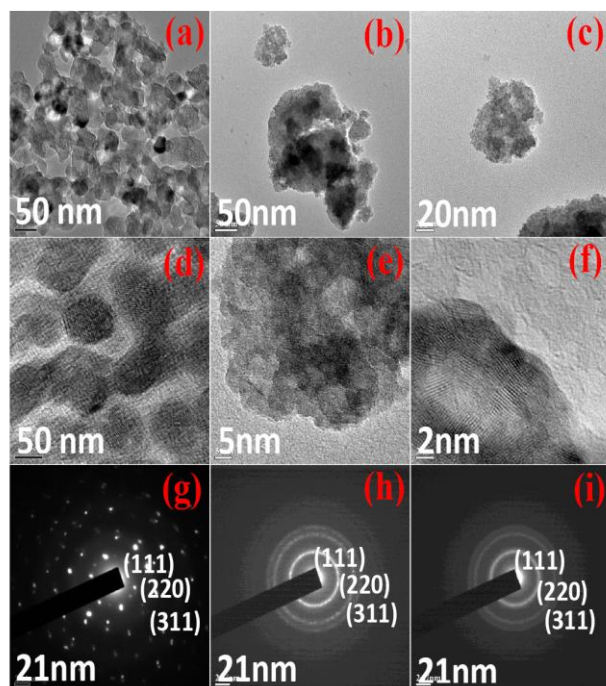


Fig. 3. (a)-(c) TEM images, (d)-(f) HR-TEM images and (g)-(i) SAED images of pure and $Zn_{1-(x+y)}Mn_xNi_yS$ ($x=1, 3, 5$ mol % at $y=3$ mol % constant) nanoparticles.

Photoluminescence (PL) studies

PL spectra of a substance gives primarily the information of its surface states [24-26]. **Fig. 4** shows the un-doped and doped ZnS nano particles with excitation wavelength 306 nm. All the samples give rise to blue emission peak at about 438 nm. This is due to the recombination of surface donor level and zinc acceptor level as given in literature [27]. For (Mn, Ni) nanosamples, five peaks at 450 nm, 467 nm, 481 nm, and 492 nm and a weak emission peak at 619 nm are observed. Those observations indicate different PL centers.

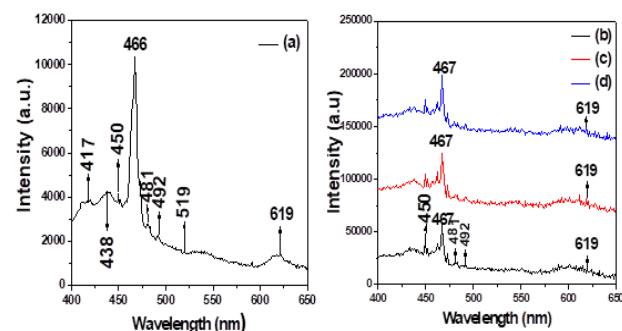


Fig. 4. PL images of (a) un-doped ZnS, and (b) 1 mol% doped Mn, (c) 3 mol % doped Mn, (d) 5 mol% doped Mn with 3 mol% of Ni into ZnS nanoparticles.

Magnetic properties

Fig. 5 shows the magnetic behavior of pure ZnS and $Zn_{1-(x+y)}Mn_xNi_yS$ ($x=1, 3, 5$ mol % at $y=3$ mol % constant) nanoparticles. Room temperature Hysteresis curve (-15,000 to +15,000 G) is studied using VSM. Pure ZnS nanoparticles do not exhibit the ferromagnetism at room temperature due to the absence of un paired electrons in its 'd' orbital.

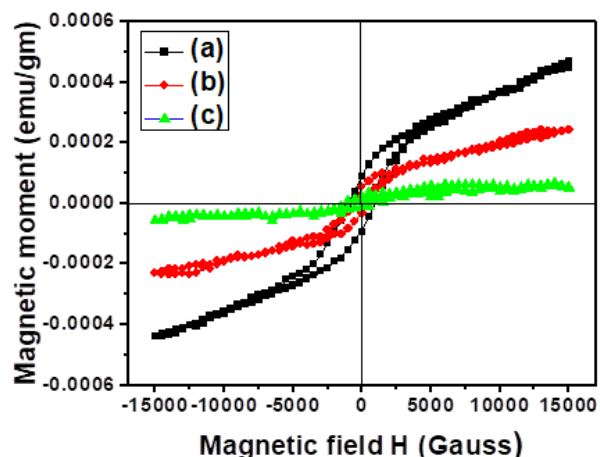


Fig. 5. Hysteresis loop of (a) 1 mol % doped Mn, (b) 3 mol % doped Mn, (c) 5 mol % doped Mn with 3 mol % of Ni in to ZnS nanoparticles.

Table 3. Magnetization, coercivity and retentivity values of (Mn, Ni) co-doped ZnS nanoparticles.

Sample	Ms (emu)	Coercivity (G)	Retentivity (emu)
1% Mn and 3% Ni	453.86×10^{-6}	960.069	2.278×10^{-6}
3% Mn and 3% Ni	239.58×10^{-6}	505.99	43.804×10^{-6}
5% Mn and 3% Ni	62.142×10^{-6}	1022.9	5.474×10^{-6}

The magnetization curves are observed for all (Mn, Ni) co-doped nano particles. Magnetic properties arise from defect sites and spin polarized magnetic moments are due to the above. The ferromagnetic behavior decreases with increase of different doping of Mn content, as noted in **Table 3**. The Mn and Ni in substitutional Zn sites give rise to DAP (Donor-Acceptor Pair) recombination [28].

Conclusions

Un-doped and doped ZnS nanopowders are synthesized by co-precipitation method. The XRD results exhibits Cubic blended structure for all prepared samples. The surface morphology, elemental composition and size of the powders are studied using SEM, EDAX and TEM analysis. Crystalline sizes obtained from TEM agree well those of XRD results. PL spectra show blue emission peak at around 467 nm. M-H measurements at room temperature for (Mn, Ni) co-doped ZnS nanoparticles, show ferromagnetism and the saturation

magnetization decrease with the increasing of Mn concentration.

Acknowledgments

The authors are grateful to our former teacher and retired professor Y. Prabhakara Reddy, Department of Physics, S.V. University for the encouragement and suggestions in our research work.

References

1. L.E. Brus, *J. Phys. Chem.*; **1984**, *80*, 4403.
2. Y. Wang, N. Herron, *J. Phys. Chem.*; **1991**, *95*, 525.
3. N.A. Dhas, A. Zaban, A. Gedanken, *Chem. Mater.*; **1999**, *11*, 806.
4. R. Vacassy, S.M. Scholz, J. Dutta, H. Hoffmann, C.J.G. Plummer, G. Carrot, J. Hilborn, M. Akine, *Mater. Res. Soc. Symp. Proc.*; **1998**, *501*, 369.
5. P. Calandra, M. Goffred, V.T. Liveri, *Colloids Surf. A* **1999**, *160*, 9.
6. O. Agyeman, C.N. Xu, M. Suzuki, X.G. Zhang, *J. Mater. Res.* **2002**, *17*, 959.
7. C.N. Xu, T. Watababe, M. Akiyama, X.G. Zhang, *Appl. Phys. Lett.* **1999**, *74*, 1736.
8. Ashish K. Keshari, Avinash C. Pandey, *J. Appl. Phys.* **2009**, *105*, 064315.
9. R.N. Bhargava, D. Gallagher, T. Welker, *J. Lumin.* **1994**, *275*, 60.
10. Y. Li, Y. Ding, Y. Zhang, Y. Qian, *J. Phys. Chem. Solids*, **1993**, *60*, 13.
11. J.F. Suyver, S.F. Wuister, J.J. Kelly, A. Meijerink, *Nano Lett.* **2001**, *1*, 42.
12. Hui Li, Y. Wan, Wei-Heng Shih, *Nanotechnology* **2007**, *18*, 205604.
13. Mingwen Wang, Lingdong Sun, Xuefeng Fu, Chunsheng Liao, Chunhua Yan, *Solid State Comm.* **2000**, *115*, 493.
14. Ageeth A. Bol, Joke Ferwerda, Jaap A. Bergwerff, Andries Meijerink, *J. Lumin.* **2002**, *99*, 325.
15. Rajesh Sharma, H.S. Bhatti, *Nanotechnology* **2007**, *18*, 465703.
16. Hemant Soni, Mukesh Chawda, Dhananjay Bodas, *Mater. Lett.* **2009**, *63*, 767.
17. Ageeth A. Bol, Rick van Beek, Andries Meijerink, *Chem. Mater.* **2002**, *14*, 1121.
18. J.Z. Liu., P.X. Yan, G.H. Yue, J.B. Chang, D.M. Qu, R.F. Zhuo, *J. Phys. D: Appl. Phys.* **2006**, *39*, 2352.
19. Kewei Liu, J.Y. Zhang, Xiaojie Wu, Binghui Li, Dezhen Shen, *Physica B* **2007**, *389*, 248.
20. Ping Yang, Mengkai Lu, Dong Xu, Duorong Yuan, Chunfeng Song, *J. Phys. Chem. Solids* **2003**, *64*, 155.
21. Subhajit Biswas, Soumitra Kar, *Nanotechnology* **2008**, *19*, 045710.
22. Sameer Sapra, J. Nanda, A. Anand, S.V. Bhat, D.D. Sarma, *J. Nanosci. Nanotech.* **2003**, *3*, 392.
23. B.D. Cullity, in: *Elements of X-ray Diffraction*, Addison-Wesley, Reading, MA, **1978**.
24. W. Chen, Z.G. Wang, Z.J. Lin, L.Y. Lin, *J. Appl. Phys.* **1997**, *82*, 3111.
25. T. Arai, T. Yoshida, T. Ogawa, *J. Appl. Phys.* **1987**, *62*, 396.
26. M. Agata, H. Kurase, S. Hayashi, K. Yamamoto, *Solid State Commun.* **1990**, *76*, 1061.
27. Huaming Yang, Chenghuan Huang, Xiaohui Su, and Aidong Tang, *Journal of Alloys and Compounds*, **2005**, *402*, 1.
28. M. Ragam, N. Sankar, K. Ramachandran, *Defect Diffus. For.* **2011**, *318*, 11.