GE-International Journal of Engineering Research
Vol. 5, Issue 6, June 2017 Impact Factor- 5.613
ISSN(O): 2321-1717, ISSN(P): 2394-420X
© Associated Asia Research Foundation (AARF) Publication
Website: www.aarf.asiaEmail : **editor@aarf.asia , editoraarf@gmail.com**

STUDIES OF MN^{2+} DOPED CDS NANOPARTICLES UNDER OPTIMIZED ANNEALING CONDITION

S. Rinu Sam

Sivaji College of Engineering and Technology, Manivila, Tamil Nadu, India.

ABSTRACT

The synthesis of CdSnano particles was widely studied for their potential usage in the field of optics. Semi conductor nanoparticles doped with transition metal ions have attracted wide attention due to their excellent luminescent properties. The transition metal doped nanoparticles shows different optical properties corresponding to their host counter parts. These nano particles have tremendous applications in optical light emitting diodes. The synthesis of pureCdSnano particles and CdS with transition metal ion(Mn^{2+})doping was done by microwave assisted solvothermal method. The prepared nanocrystals were characterized by XRD,SEM,EDAX andICP-AES of the samples are recorded and discussed briefly.

Key words:nanoparticles; solvothermal; doping; XRD; SEM; EDAX; AES

1. Introduction

Nanometer sized semiconductor particles belong to a state of matter in the transition region between molecules and solids. During the past two decades, research on quantum size semiconductor particles has increased enormously due to their exciting novel properties [1-4]. II–VI group semiconductor nano materials arepresently of great interest for their practical applications such as zero-dimensional quantum confined materials and for their applications in optoelectronics and photonics. Numerous reports are available in the literature on synthetic techniques chalcagenides with solvothermal method[5-15]. Recently, the solvothermal process as a powerful method for the synthesis of materials has attracted tremendous

attentions[16,17]. Comparing with the synthesis route based on colloid chemistry, this method takes the advantage of obtaining pure and clean nanoparticles in high degree of crystallinity. CdS is animportant semiconductor and has many optoelectronic applications including solar cells, photodiodes, light emitting diodes, nonlinear optics and heterogeneous photocatalysis. In this paper we choose thioacetamide as the sulphide source. It is much easier for thioacetamide to release sulphide ions. A micro wave oven has been used for heating the solution containing the reactants and the effect of annealing and dopants on the physical properties of CdS nanoparticles have been analysized.

2. Experimental Method

2.1 Solvothermal synthesis of pure and doped CdSnano particles

To prepare Pure CdS nanoparticles by microwave-assisted solvothermal route, cadmium acetate ($Cd(CH_3COO)_2.2H_2O$) and thioacetamide (CH_3CSNH_2) were taken as the starting precursor materials in 1:1 molar ratio. The precursor materials were dissolved in ethylene glycol and stirred well using a magnetic stirrer. The well-mixed solution was taken in a bowl and it was kept in a domestic microwave oven (Videocon 800 W model provided with six stage adjustable power/time domain). The apparatus is fully loaded with rotating hard glass circular plate at the bottom to place the bowl on it. The side wall of the apparatus is well protected with tin sheet cover. The solution is placed into the bowl with top cover which is sustainable for the heat produced inside the oven. The solution/material was subjected to microwave irradiation of 800 W for 20 minutes.

The colloidal precipitate obtained after this irradiation was air cooled to room temperature. This cooled substance was washed several times using doubly distilled water and then with alcohol to remove the organic impurities, if any, present in the sample. The sample was then filtered and dried in atmospheric air and collected as the yield. The sample was finally annealed at about 100 ºC for 2 hours to get phase-pure nanoparticles of CdS and the sample is called Sample A.

As grown CdS nanoparticles are annealed for 200^0C for different duration namely 12 minutes, 20 minutes and 120 minutes. These are termed as Sample 1, Sample 2, Sample 3 respectively. As prepared CdS nanoparticles are annealed at different temperature namely 100^0C, 200^0C and 300^0C for 120 minutes. These samples are named as sample A, sample B and sample C.

In order to synthesizeCdS: Mn^{2+} nanoparticles, 1 mol%, 2 mol% and 3 mol% of manganese acetate were added to the solution of cadmium acetate (Cd $(Ac)_2$) and thioacetamide (TAA), under the solvothermal process and these samples were annealed at about 100 ºC for 2 hours. Let the manganese doped CdS samples be called as Sample B1,Sample B2 and Sample B3.

3 RESULT AND DISCUSSION

3.1 Powder XRD of Pure CdS nanoparticles

The powder XRD result of pure CdS nanoparticles are shown in the fig.1.The XRD pattern consists of there are three distinct peaks at three different angles. It is also observed that there is a small fourth peak. It shows that the synthesized sample belongs to pure CdS phase. All the XRD peaks are broadened and diffused. This Broad and diffused pattern of XRD lines are indicative of the nanocrystalline nature of CdS particles. It contains cubic phase with a little hexagonal phase of CdS. Cubic CdS phase was most often found in synthesized colloidal CdS particles, but the macroscale phase of CdS is normally with the hexagonal structure [18]. In solvothermal synthesis, the hexagonal phase is more common [19,20]. The coexistence of cubic and hexagonal phases has also been reported [21]. We also obtain cubic phase as well as hexagonal phase in the present system. The 'hkl' values are compared with the standard JCPDS file (10-454) [22]. The XRD pattern exhibits prominent, broad peaks at 2θvalues of 26.40 Å, 43.73 Å and 51.90 Å which could be indexed to scattering from (1 1 1), (2 2 0) and (3 1 1) planes respectively of cubic CdS [23-30]. The fourth peak at 2θvalue of 70.01 Å which is indexed to scattered at (4 0 0) plane shows the hexagonal phase.

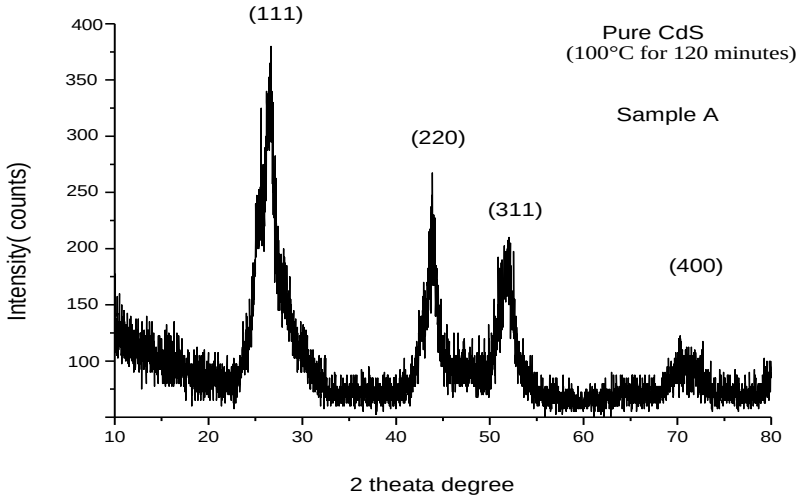


Figure 1: XRD pattern for Pure CdS nanoparticles

Standared JCPDS			Experimental values		
(hkl)	**d-pacingÅ**	**2θ (degrees)**	**(hkl)**	**d-spacing Å**	**2θ (degrees)**
(111)	3.16	28.218	(111)	3.34	26.66
(220)	1.93	47.046	(220)	2.06	43.78
(311)	1.64	56.029	(311)	1.75	51.95
(400)	1.36	68.999	(400)	1.48	70.01

Table 1: Comparison between experimental and standard XRD data

The XRD peaks are found to be very broad indicating very fine size of the grains of the sample. This broadening of the peak could also arise due to the micro-straining of the crystal structure arising from defects like dislocation and twinning etc. These defects are believed to be associated with the chemically synthesized nanocrystals as they grow spontaneously during chemical reaction [31,32]. These nanocrystals have lesser lattice planes compared to bulk, which contributes to the broadening of the peaks in the diffused pattern. It shows that the nanocrystalline nature of CdS particles and the diffused pattern shows the presence of cubic phase as well as hexagonal phase in the present system. The lattice parameter values were calculated using XRDA software and the values are found to be a = b = c = 5.4500 Å. All the data obtained in this work are well matched with the standard values as shown in the table 1.

3.2 Effect of annealing time on particle size

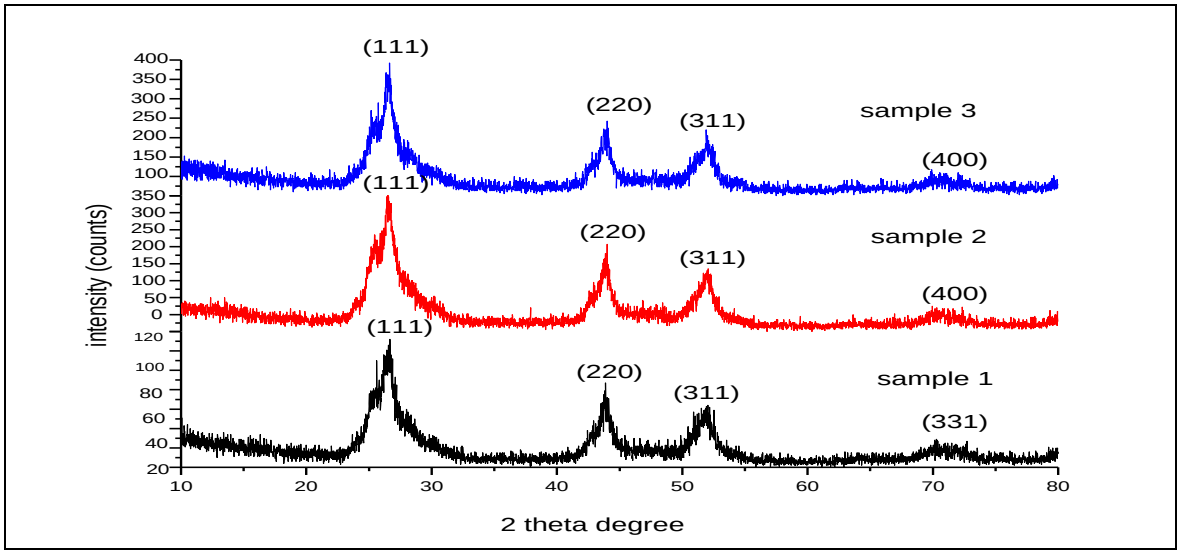


Fig 2 : - The XRD patterns of pure CdS due to the effect of annealing time

Name of the sample	Temperature (^{0}C)	Annealing time(min)	Peak height (count)	Angle (2 Theta) (111),(220),(311) Å	Particle size (nm)
Sample 1	200^{0}C	12	121.32	26.53,43.83, 51.83	14.06
Sample 2	200^{0}C	20	328.47	26.57,43.90,51.98	18.33
Sample 3	200^{0}C	120	403.74	26.66,43.94,52.02	21.05

Table: 2: The size of the pure CdSnano particles due to annealing time

From the figure 2 as grown CdS nanoparticles are annealed for 200^{0}C for different duration namely 12 minutes, 20 minutes and 120 minutes respectively. The XRD pattern shows three distint peaks at different angles, which emphasizes that the synthesized samples are in pure CdS phase. In the figure, one smaller peak is also present and all the four peaks are broadened and diffused. It can be concluded that all the CdS samples are in nanocrystalline form and are exhibited in the broadened and diffused pattern of XRD lines. The XRD pattern exhibits prominent 'hkl' values and these values are compared with standard JCPDS file. The peaks are indexed at (111), (220), (311) and (400) planes and from the diffused and broadened XRD pattern, one could substantiate that the nanoparticle is in cubic as well as hexagonal phases. The figure indicates that, as the annealing time increases, the diffraction peaks become sharper and narrower which tells us the crystalline nature of the CdS nanoparticles and the increase in intensity indicates the intensification in crystallinty[33].

3.3 Effect of annealing temperature on particle size

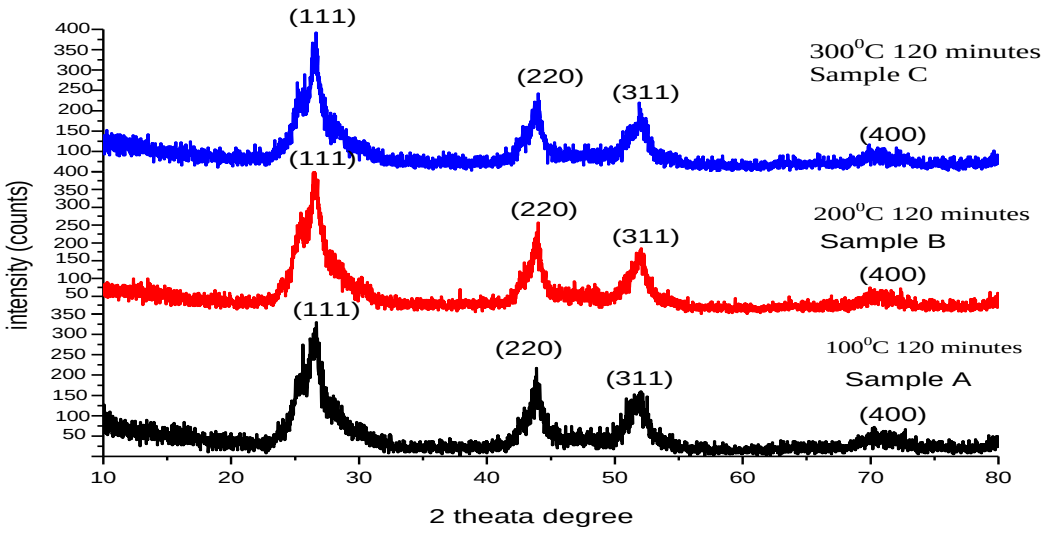


Fig 3 : - The XRD patterns of pure CdS due to the effect of annealing temperature

As prepeared CdS nanoparticles are annealed at different temperature namely 100^0C, 200^0C and 300^0C for 120 minutes are shown in the figure 3respectively. The different parameters from the XRD and the particle size calculated from Sherrer's formula are given in table 3for the samples. It shows that four distinct peaks in different angles. Moreover all the peaks are broadened and diffused. As the annealing time and temperature increases, the diffraction peaks become sharper and narrower, and the intensity increases which indicates that the intensification in crystallinity [33].These are indicates that all the samples are in nanocrystalline nature. The broadened and diffused nature of the peaks establishes the existence of cubic as well as hexagonal nature of the Pure CdS nanoparticles.

From the figure 3, it is also observed that the peak intensity increases with increase in annealing temperature for all the samples. The increase in intensity with temperature may be due to the crystalline nature of the Pure CdS nanoparticles. A slight shift is also observed towards the higher angle region as the temperature increases. Moreover, the peak width is found to decrease with the annealing temperatures. All these observations explain the crystalline nature of pure CdS nanoparticle.

The particle size of the Pure CdS nanoparticle is found to increase with the annealing temperature. In heating process when the particles are formed, they collide and either coalesce with one another to form a larger particle or coagulate [34]. The process which occurs depends upon the temperature and available energy, that's why particle size increases with increasing temperature.

Name of the sample	Temperature (^{0}C)	Annealing time (min)	Peak height (count)	Max Peak (2 theta) (111),(220),(311), (400)	FWHM (^{o}2θ)	Particle size (nm)
Sample A	100^{0}C	120	370.67	26.40,43.73,51.90, 70.01	0.2676	16.65
Sample B	200^{0}C	120	403.74	26.66,43.78,51.93, 70.08	0.4684	21.05
Sample C	300^{0}C	120	410.24	26.68,43.94,51.95,70. 13	0.4587	23.36

Table: 3: The size of the pure CdSnano particles due to annealing temperature

3.4 Powder XRD of Doped CdS nanoparticles

In this study pure CdS is doped with the transition metal ion of Mn^{2+} for different concentration, they are 1 mol%, 2 mol% and 3 mol% respectevily. And the samples are named as sample B1, sample B2 and sample B3. All these sampleas are annealed at 100^{0}C for 120 minutes and its XRD patters are shown in the figure 4.

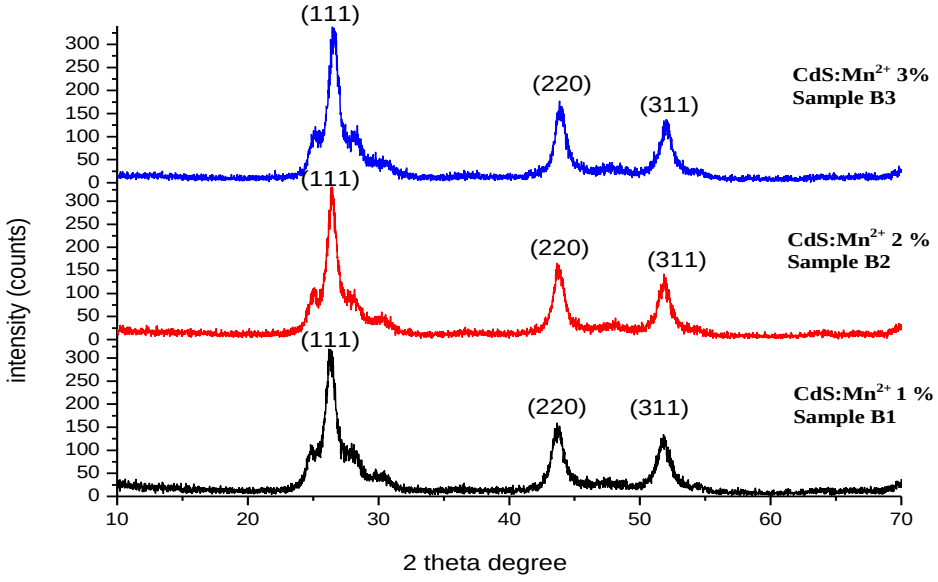


Fig 4:- The XRD patterns of Mn^{2+} doped CdSnano particles

In the figure 4 all the XRD peaks of doped samples are broadened and clear to visible. It gives that, with increased doping concentration of Mn^{2+} ion the intensity of the diffraction peaks increase and full width at half maximum(FWHM) is gradually increased. The increase

of doping concentration results the decrease of crystallinty and increase of disorder effect which resulted in the broadening and increase of intensity of the XRD peaks. The analysis of XRD reveals that Cds:Mn^{2+} nanocrystals have zinc-blende crystal structure. It is clearly seen that all the XRD patterns correspond to cubic structure of CdS.

In this XRD pattern peaks for the doped metal ions, sulphides or any binary metal phase are absent. The peak positions are slightyshifited to the lower angles with the increment of doing percentage. This indicates the slight increment of lattice parameters. This is due to the presumable results from the substitution of metal ions having a small ionic radius. When the doping concentration has increased, the particle size of the nanocrystal decreased, as shown in the table 4.

The grain size of the pure nanocrystallineCdS was calculated from the Scherrer's equation [16-19]. The Scherrer's formula is given by:

$$D = 0.9\lambda/\beta Cos\theta$$

Where D is the crystallite size in nm, λ is the wavelength of the X-rays (1.5406 Å), β is the full width at half maximum and θ is the diffraction peak angle.

Concentration	**Peak height (count)**	**Maximum Peak Value of 2θ for(°2θ)**	**FWHM (°2θ)**	**Particle size (nm)**
Pure Cds	370.67	26.40	0.2676	16.65
(Mn^{2+} 1%) Sample B1	347.85	26.39	0.5385	14.93
(Mn^{2+} 2%) Sample B2	331.16	26.33	0.6528	14.06
(Mn^{2+} 3%) Sample B3	325.69	26.25	0.6691	12.12

Table: 4:- Maximum 2θ values of pure and doped samples

3.5 Effect of concentration on dopedCdSnano particles

The effect of ionic radius of the dopants in the pure CdS nanoparticle is studied in this section. The various parameters observed from the XRD of pure and doped CdS: Mn^{2+} for 1 mol %, 2 mol % and 3 mol % are tabulated in tables 5. For all the above samples, the annealing temperature and time is kept at 100 ^{0}C for 120 minutes.

From table 5, it is observed that the intensity of the dopant is found to be decreasing with the increase of the concentration of the dopent. As the concentration of the dopent increases, the intensity count of the spectrum and the d-spacing between the peaks are found to be decreasing, thereby confirming the more and more crystalline nature of the pure and doped CdS nanoparticles. The *d* spacings of the Mn^{2+} doped CdS nanoparticles in the range of 355-339 pm, which indicate the expansion occurs after doping for (111) peak. In contrast, shrinkage was occurred for other peaks also. The different changes in the microstructure infer that two kinds of species might exist in the doped CdSnano particles [35].

Mn^{2+} Ionic radii 72	**For 1mol % Attributes**	**For 2mol % Attributes**	**For 3mol % Attributes**	**Pure CdS Ionic radii 109**
Intensity	347.85	331.16	325.69	370.67
FWHM	0.5385	0.6528	0.6691	0.2676
2θ	26.39	26.33	26.25	26.40
Particle size	14.93	14.06	12.12	16.65
d- spacing	3.394	3.389	3.346	3.343

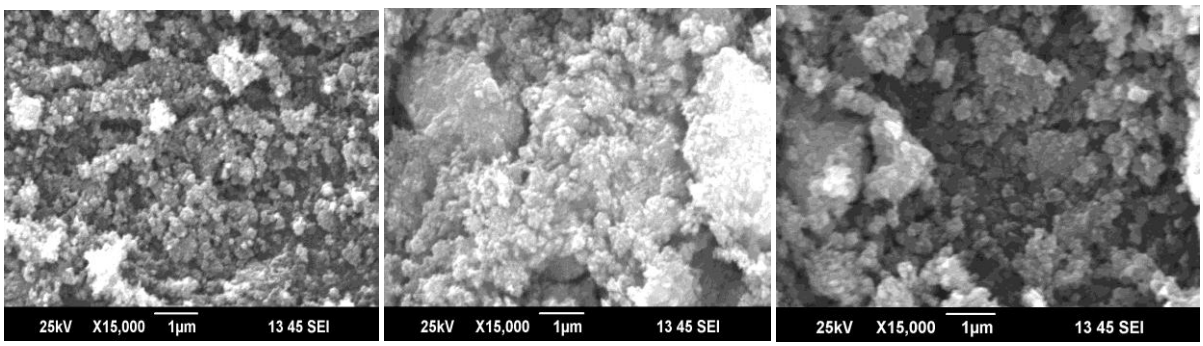
Table: 5:- Effect of ionic radii on pure and doped samples

3.6Scanning Electron Microscopic (SEM) studies

The morphologies of the as-prepared samples were investigated through Scanning Electron Microscopic (SEM) images. The SEM images were taken for the nanopowdered samples prepared by the present solvothermal method. Figure 5 shows the SEM images ofMn doped nanoparticles. The rough and spongy surface morphology is evident which makes it difficult to estimate the crystallite size due to agglomeration of the particles [36].

By this SEM technique, the grain size of the particle, shape, texture and surface properties are observed. The SEM images of all the figures shows the hexoganal phases and cubic phases of CdSnano particles. Nano-size grains and micron size splashed particles can

be determined from the result of the SEM micrograph [37]. By adding Mn^{2+} impurity to the target will increase the size of the grains and its proved by their background layer presented in the SEM image. The average particle size is found to be around 12.9 nm- 14.9 nm.



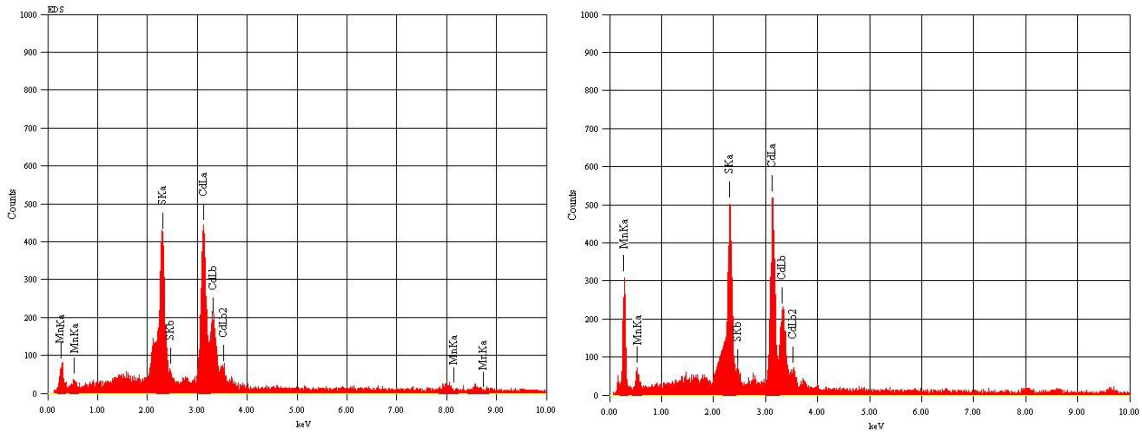
CdS:Mn^{2+}1mol % (sample B1) CdS:Mn^{2+}2mol % (sample B2)CdS:Mn^{2+}3mol % (sample B3)

Fig.5 : SEM images of doped CdS nanoparticles

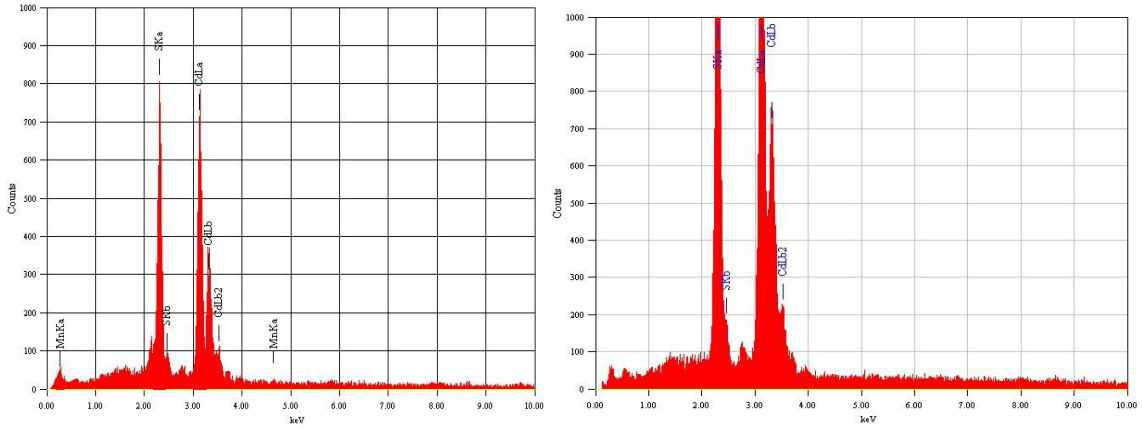
3.7Energy Dispersive X-ray Analysis (EDAX) of as-prepared samples

Figure 6 shows the energy dispersive X-ray (EDAX) spectra of the pure and Mn doped CdS nanoparticles. The elements such as Cd, S and Mn are identified from the samples. The interest in the Mn^{2+} doped CdS is based on their outstanding magneto-optical properties caused by a strong s, p- d exchange interaction between electron / hole band states and Mn^{2+} 3d- electron states.

From the table 6 one could easily understand the presence of Cadmium, Sulphide and the presence of doping element, because Cd,S and Mn elements are to be in a stoichiometric atomic ratio on EDAX pattern. From the table, it is clear that the dopant is included in the CdS nanoparticles. As the concentration increases, the percentage of dopant also correspondingly increase. The atomic percentages of the chemical species are found in the Table 6. The average deviation of the estimated compositions from the target compositions is within ±2.5%.



CdS:Mn^{2+}1mol % (sample B1) **CdS:Mn^{2+}2mol % (sample B2)**



CdS:Mn^{2+}3mol % (sample B3) **Pure CdS**

Fig.6: EDAX images of pure and doped CdS nanoparticles

Starting elements (At %)			EADX Analysis (At%)		
Mn	Cd	S	Cd	S	Mn
0	50	50	47.58	52.42	0
1	49	50	47.02	51.97	1.01
2	48	50	46.38	51.59	2.03
3	47	50	46.12	50.89	2.99

Table 6: Quantitative elements for pure and CdS:Mn^{2+} nanoparticles

3.8Atomic Emission Spectroscopy (AES)

The given sample is digested with HNO3 and analyzed with ICP-AES system. The below ICP-AES result shows that sample contains 46.82% ppm of pure Cd particles and 53.18 % ppm of S particles. In all the AES sample result, it shows that they are in stoichiometric atomic ratio. The percentages of the chemical species found in the pure CdS and doped samples are given in the table 7.

Sl. No.	sample	CdS:Mn^{2+}	Cd ppm	S ppm	Mn pm
1	Pure	**Pure**	46.82	53.18	-
2	B1	**1%**	46.03	52.93	1.04
3	B2	**2%**	45.91	52.06	2.03
4	B3	**3%**	45.57	51.43	3.00

Table: 7. ICP- AES compositional analysis of the samples.Cds:Mn^{2+}

4. Conclusion

In this work we have demonstrated that a versatile process of microwave solvothermal synthesis of nano crystalline leads to fast, simpler and energy efficient technique. From the above result we can conclude that the cubic as well as hexogonal phase CdSnano particle can be fabricated through a solvothermal process with ethylene glycol as the solvent and thioacetamide as the sulphide source. Here we find that the annealing effect had increased the crystalline size of theCdSnano particles. Moreover, the particle size of the metal ion doped nano particles increases with the concentaration. The presence of the dopants is confirmed by the EDAX and AES studies. The atomic percentages of the chemical species found by EDAX analysis. The average deviation of the estimated compositions from the target compositions is within ±2.5%. The hexagonal and cubic structures were seen by SEM images. The average particle size is found to be around 16nm.

Acknowledgment

The authors like to thank the staff members of NPCILKudankulam, Tamil Nadu, IIT Chennai, STIC Cochin University, SRM university Chennai, CSIR- RRL Trivandram, Kerala for the help rendered to carry out this work.

References

[1] LBrus, *J. Phys. Chem*. **90**, 2555 (1986)

[2] AHengelin, *Chem. Rev*. **89**, 1861 (1989)

[3] H Weller, *Adv. Mater*. **5**, 88 (1993)

[4] A P Alivisatos, *Science***271**, 933 (1996)

[5] C. L. CAHILL, B. GUGLIOTTA and J . B. PARISE, *Chem.Commun*. **16** (1998) 1715.

[6] M. SCHUR, and W. BENSCH, , *Z. Anorg. Allg. Che.* **624** (1998) 310.

[7] G. C. GUO, R. M. W. KWOK and T. C. W. MAK,*Inorg.Chem. Soc.***36** (1997) 2475.

[8] C. REISNER and W. TREMEL,*Chem.Commun*. **4** (1997) 387.

[9] Y. LI, Y. DING, Y. QIAN, Y. ZHANG and L. YANG, *Inorg. Chem*. **37** (1998) 2844.

[10]J. HU, Q. LU, K. TANG, Y. QIAN, G. ZHOU and X. LIU,*Chem.Commun*. **12** (1999) 1093.

[11] X. QIAN,X. ZHANG, C. WANG, Y. XIE and Y. QIAN,*Inorg.Chem.* **38** (1999) 2621.

[12] W. WANG, Y. GENG, P. YAN, F. LIU, Y. XIE and Y. QIAN, *J Am.Chem. Soc.***121** (1999) 4062.

[13] W. WANG, P. YAN, F. LIU, Y. XIE, Y. GENG and Y. QIAN, *J Mater.Chem.* **8** (1998) 2321.

[14] S. YU, J. YANG, Y. WU, Z. HAN, J. LU, Y. XIE and Y. QIAN, *ibid.* **8** (1998) 1949.

[15]W. HORST, *Ang. Chem. Int. Ed. Engl*. **32** (1993) 41.

[16] G. DEMAZEAU, *J.Mater. Chem*. **9** (1999) 10.

[17] M. SCHUR, H. RIJNBERK and C. NATHER, *Polyhedron***18** (1998) 101.

[18] W. Horst, Ang. Chem. Int. Ed. Engl., vol.**32** (1993), 41.

[19] Y. Li, H. Liao, Y. Fan, L. Li, Y. Qian, Mater. Chem. Phys., vol.**58** (1999), 87.

[20] Y. Li, H. Liao, Y. Ding, Y. Fan, Y.Zhang And Y. Qian ,Inorg. Chem., vol.**38** (1989) 1283.

[21] S. Yu, J. Yang, Y. Wu, Z. Han, J. Lu, Y. Xie, Y. Qian, *Mater. Chem*., vol.**9** (1999), 1283.

[22] H.C. Warad, S.C. Ghosh, B. Hemtanona, C. Thanachayanont, J. Dutta, *Science And Technology Of Advanced Materials*., vol.**6** (2005), 296.

[23] Xin Chang, Jieming Cao, HongmeiJi, Baoqing Fang, Jie Feng, Lijia Pan, Fang Zhang, Haiyan Wang, *Materials Chemistry and Physics*., vol.**89** (2005), 6.

[24] A. J. Bisquert, G. Garcia-Belmonte, A. Pitarch, H.J. Bolink, *Chem. Phys.Lett*.,vol.**422** (2006), 184.

[25] W. Wang, I .Germanenko,M. Samy El-Shall, *Chem. Mater*.,vol.**14** (2002), 3028.

[26] M. Shao, Q. Li, L Kong, W .Yu, Y. Qian, *J. Phys. Chem*. Solids., vol.**64** (2003), 1147

[27] R. Devi,P. Purkayastha,P.K. Kalita And B. Sarma, *Sci*., vol.**30 (**2007), 123-128.

[28] El Bially A.B, Seoudi R, EisaW.Shabaka A.A, Soliman S.I , Abd El Hamid R.K R.A Ramadan, *Jul Of ApplSciRech*., vol.**8(2**) (2012), 676-685.

[29] Aneeqa Sabah, Saadat Anwar Siddiqi, Salamat Ali, *World Academy Of Science*., vol.**45** (2010).

[30] K. Manickathai, S. KasiViswanathan, M. Alagar, *Ind. J. Pure & Appl. Phys*., vol.**46** (2008),561-564.

[31] A.Dumbrava, C. Badea, G. Prodan and V. Ciupina, *Chalcogendieltrs*., vol.**7** (2010),111-118.

[32] Wenzhong Wang, Zhihui Liu, Changlin Zheng, Congkang Xu, Yingkailuiguanghou Wang, *Matrls lets* (2002).

[33]E.Wu, Powd, An Interactive Powder Diffraction Data Interpretation And Indexing Program Ver.2.1, *School Of Physical Science,* Flinders University Of South Australia,Bedford Park S.A, 5042 Au

[34] M. Z. Iqbal, S. Aliand M. A. Mirza . CodenJnsmac., vol. **48**, No.1 & 2 ,(2008).

[35] Sue-Min Chang And Ruey-An Doong, *J.Phys.Chem*. ,B,(2004),108.

[36] P. Venugopal, K. Ravichandran, *Adv. Mat. Lett.*, vol.**4(1)** (2013) 200-206.M.

[37] S.M. Mahdavi, A. Irajizad, A. Azarian, R.M. Tilaki, *Science Iranica.*,vol**15** (2008) 360-365.