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X-RAY DIFFRACTION AND TRANSMISSION ELECTRON MICROSCOPY STUDIES ON NICKEL DOPED CdS NANOPARTICLES

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In the present work, conventional chemical co-precipitation method was employed for the preparation of Ni (2%,4%,6%,8% and 10%) doped CdS nanoparticles. XRD studies reveal that Ni doped CdS crystallizes in single phase hexagonal structure with particle size distribution of 21-23nm. In Ni doped CdS samples, the lattice parameters are observed to decrease with increase of Ni concentration. A detailed systematic study on Ni doped CdS sample is done by characterizing X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM).

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1. Introduction

II-VI semiconducting chalcogenide nanoparticles, especially sulfides and selenides have been investigated extensively, owing to their interesting opto-electronic properties [1]. CdS has been extensively studied due to its potential technological applications in filed effect transistors, solar cells, photovoltaic, light emitting diodes, photocatalysis, photoluminescence, infrared phototdetector, environmental sensors and biological sensors [2-8]. In particular, transition metal(TM) doped semiconductors, known as diluted magnetic semiconductors, have attracted widespread scientific attention due to their prospective applications in magneto-optical and spintronic devices [9, 10]. Recently TM doped CdS thin films and nanostructures have been shown to exhibit interesting properties viz. bistable switching [11], ferromagnetism [12, 13], and tunable photoluminescence [14, 15]. Transition metal doping, in particular diminishes the quantum yields in the visible and near-band-gap region by acting as a quenching or killer centers for fluorescence and photoconduction, and results in short carrier lifetimes useful in fast optoelectronic devices[16-18]. These findings opened additional avenues for further development of advanced devices based on TM-doped CdS. Growth of TM-doped CdS has been demonstrated by various physical and chemical methods [11-17]. In the present study we have synthesized Ni doped CdS nanoparticles through chemical co-precipitation technique. Ni doped CdS nanoparticles are extensively studied using X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM).

2. Experimental

Ni doped CdS nanoparticles were prepared by colloidal chemical co-precipitation method using Cadmium acetate, Sodium sulfide and Nickel acetate as starting compounds. Appropriate quantities of these were weighed in microbalance (M/s SICO, India) according to the stoichiometry to obtain 2,4,6,8 & 10 at% target dopant concentrations and were dissolved in 100ml

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of methanol to make 0.1M solutions. The stoichiometric solution was taken in a burette and was added in drops with continuous stirring to a mixture of Na_2S(0.1M) + 50ml of H_2O + 1.1ml of thiophenol + 100ml of methanol until fine precipitate of CdS:Ni was formed. After complete precipitation, the solution in conical flask was constantly stirred for about 20h. Then the precipitates were filtered out separately and washed thoroughly with de-ionized water. Finally these samples are subjected to sintering process. The green colored nanocrystalline CdS: Ni^{2+} powders were obtained. The samples were calcined at 300°C/2hrs in vacuum. X-ray diffraction (XRD) measurements have been performed to know the structure and phase of the sample using Bruker AXS D8 advance model PW 1600, powder X-ray diffractometer using CuK_α (λ =0.15406nm) has been used as the source of X-rays. The morphology and particle size of samples were determined by transmission electron microscopy (TEM). Bright field images and Selected Area Electron Diffraction (SAED) patterns of the sample are performed on Philips CM 120 ST transmission electron microscope operated at 100 kV, with 2Å resolution.

3. Results and discussion

Figure 1 shows X-ray diffraction patterns of Ni (2, 4, 6, 8 & 10 at. %) doped CdS. The six main diffraction peaks are corresponding to (0 0 2), (1 0 0), (1 0 1), (1 1 0), (1 0 3) and (1 1 2) planes respectively. Analyzing the most prominent peaks, the crystal structure of these nanoparticles has been found to be in hexagonal phase. The maximum peak intensity is found for 4% Ni doped CdS. From the Full Width at Half Maximum (FWHM) of the most intense peak particle size has been calculated by using the Scherer formula [19],

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

Where λ is the wavelength of X-ray diffraction, β is FWHM in radians of the XRD peak and θ is the angle of diffraction. The average particle size (D) of the sample is found to be in the range of 21-23nm. The peaks from XRD have been indexed with the help of a computer program – POWDIN [20] using the observed interplanar spacing d. Table 1-Table 5 shows the observed and calculated values of interplanar spacing(d), lattice parameters ('a' and 'c')and volume(V) for 2%,4%,6%,8% and 10% Ni doped CdS computed from Powdin Program. The lattice constant 'a' and 'c' have been determined from interplanar spacing of different (h k l) planes. In Ni doped CdS samples, the lattice parameters are observed to decrease with increase of Ni concentration. The decrease of the lattice parameters of Ni doping is because utilize hot electrons and /or generate multiple charge carriers with a single photon.

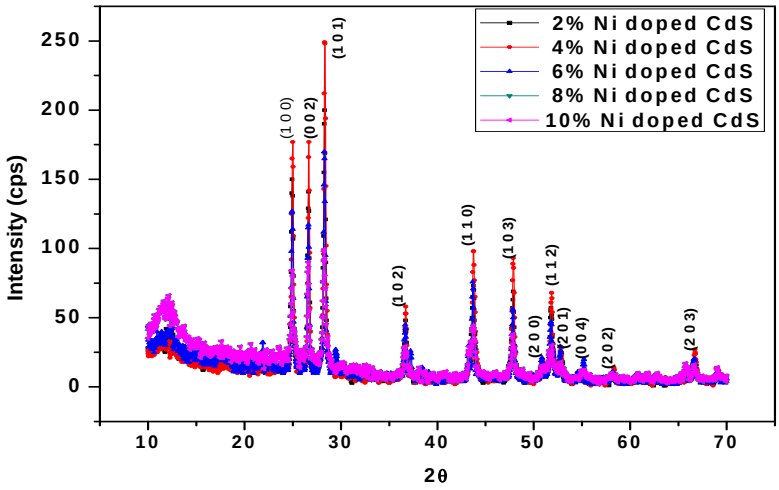

Fig 1. X-ray diffraction patterns of Ni (2%, 4%, 6%, 8% and 10%) doped CdS.

Table 1. Observed and calculated values of interplanar spacing (d) and miller indices (h k l) for 2% Nickel doped CdS.

Lattice Parameters, a= 4.119A^0, c= 6.728 A^0, c/a=1.633; Volume, V= 114.15$(A^0)^3$

Line	d-spacing A.		Indices	SinSqTheta*E4		2Theta Deg.		
o. c.	obs.	calc.	h k l	obs.	calc.	obs.	calc.	diff
1 1	3.5649	3.5879	1 0 0	466.9	460.9	24.96	24.79	.164
2 2	3.3434	3.3595	0 0 2	530.8	525.7	26.64	26.51	.130
3 3	3.1500	3.1650	1 0 1	597.9	592.3	28.31	28.17	.137
4 4	2.4464	2.4523	1 0 2	991.3	986.5	36.70	36.61	.091
5 5	2.0681	2.0715	1 1 0	1387.2	1382.6	43.73	43.66	.076
6 6	1.8989	1.8999	1 0 3	1645.3	1643.6	47.86	47.83	.026
7 7	1.7634	1.7632	1 1 2	1907.8	1908.3	51.80	51.80	-.006
8 8	1.7325	1.7333	2 0 1	1976.6	1974.9	52.79	52.77	.024
9 9	1.4019	1.4002	2 0 3	3019.0	3026.7	66.66	66.75	-.090

Table 2. Observed and calculated values of interplanar spacing (d) and miller indices (h k l) for 4% Nickel doped CdS.

Lattice Parameters, a= 4.113 A^0, c= 6.701 A^0, c/a= 1.629; Volume, V= 113.36$(A^0)^3$

Line	d-spacing A.		Indices	SinSqTheta*E4		2Theta Deg.		
o. c.	obs.	calc.	h k l	obs.	calc.	obs.	calc.	diff
1 1	3.5657	3.5879	1 0 0	466.6	460.9	24.95	24.79	.157
2 2	3.3449	3.3595	0 0 2	530.3	525.7	26.63	26.51	.118
3 3	3.1518	3.1650	1 0 1	597.2	592.3	28.29	28.17	.120
4 4	2.4475	2.4523	1 0 2	990.4	986.5	36.69	36.61	.074
5 5	2.0701	2.0715	1 1 0	1384.4	1382.6	43.69	43.66	.031
6 6	1.9001	1.8999	1 0 3	1643.2	1643.6	47.83	47.83	-.007
7 7	1.7945	1.7940	2 0 0	1842.5	1843.5	50.84	50.85	-.015
8 8	1.7639	1.7632	1 1 2	1906.8	1908.3	51.78	51.80	-.022
9 9	1.6630	1.6797	0 0 4	2145.2	2102.7	55.18	54.59	.569
10 10	1.4028	1.4002	2 0 3	3015.1	3026.3	66.61	66.75	-.139

Table 3. Observed and calculated values of interplanar spacing (d) and miller indices (h k l) for 6% Nickel doped CdS.

Lattice Parameters, a= 4.114 A^0, c= 6.702 A^0, c/a= 113.43; Volume, V= 113.43$(A^0)^3$

Line o. c.	d-spacing A. obs.	d-spacing A. calc.	Indices h k l	SinSqTheta*E4 obs.	SinSqTheta*E4 calc.	2Theta Deg. obs.	2Theta Deg. calc.	diff
1 1	3.5595	3.5879	1 0 0	468.3	460.9	24.99	24.79	.202
2 2	3.3395	3.3595	0 0 2	532.0	525.7	26.67	26.51	.162
3 3	3.1472	3.1650	1 0 1	599.0	592.3	28.33	28.17	.163
4 4	2.4454	2.4523	1 0 2	992.1	986.5	36.72	36.61	.107
5 5	2.0676	2.0715	1 1 0	1387.8	1382.6	43.74	43.66	.087
6 6	1.8984	1.8999	1 0 3	1646.2	1643.6	47.87	47.83	.039
7 7	1.7917	1.7940	2 0 0	1848.2	1843.5	50.92	50.85	.069
8 8	1.7623	1.7632	1 1 2	1910.3	1908.3	51.83	51.80	.030
9 9	1.7321	1.7333	2 0 1	1977.5	1974.9	52.81	58.77	.037
10 10	1.4011	1.4002	2 0 3	3022.4	3026.3	66.70	66.75	-0.049

Table 4. Observed and calculated values of interplanar spacing (d) and miller indices (h k l) for 8% Nickel doped CdS.

Lattice Parameters, a= 4.113 A^0, c= 6.701 A^0, c/a= 1.629; Volume, V= 113.35 $(A^0)^3$

Line o. c.	d-spacing A. obs.	d-spacing A. calc.	Indices h k l	SinSqTheta*E4 obs.	SinSqTheta*E4 calc.	2Theta Deg. obs.	2Theta Deg. calc.	diff
1 1	3.5594	3.5879	1 0 0	468.3	460.9	25.00	24.79	.202
2 2	3.3421	3.3595	0 0 2	531.2	525.7	26.65	26.51	.141
3 3	3.1489	3.1650	1 0 1	598.3	592.3	28.32	28.17	.146
4 4	2.4470	2.4523	1 0 2	990.9	986.5	36.69	36.61	.083
5 5	2.0676	2.0715	1 1 0	1387.8	1382.6	43.74	43.66	.087
6 6	1.8996	1.8999	1 0 3	1644.1	1643.6	47.84	47.83	.007
7 7	1.7615	1.7632	1 1 2	1912.0	1908.3	51.86	51.80	.054
8 8	1.7316	1.7333	2 0 1	1978.8	1974.9	52.83	52.77	.056
9 9	1.6627	1.6797	0 0 4	2146.1	2102.7	55.19	54.59	.607
10 10	1.4196	1.5213	1 0 4	2943.9	2563.6	65.72	60.84	-1.031
11 11	1.4052	1.4002	2 0 3	3004.4	3026.3	66.48	66.75	- .272
12 12	1.3594	1.3561	2 1 0	3210.4	3226.1	69.03	69.22	-.192

Table 5. Observed and calculated values of interplanar spacing (d) and miller indices (h k l) for 10% Nickel doped CdS.

Lattice Parameters, a= 4.112 A^0, c= 6.695 A^0, c/a= 1.628; Volume, V=113.2 $(A^0)^3$

Line		d-spacing A.		Indices	SinSqTheta*E4		2Theta Deg.		
o.	c.	obs.	calc.	h k l	obs.	calc.	obs.	calc.	diff
1	1	3.5651	3.5879	1 0 0	466.8	460.9	24.95	24.79	.161
2	2	3.3473	3.3595	0 0 2	529.5	525.7	26.61	26.51	.098
3	3	3.1542	3.1650	1 0 1	596.3	592.3	28.27	28.17	.098
4	4	2.4499	2.4523	1 0 2	988.5	986.5	36.65	36.61	.037
5	5	2.0685	2.0715	1 1 0	1386.6	1382.6	43.72	43.66	.066
6	6	1.9004	1.8999	1 0 3	1642.9	1643.6	47.82	47.83	-.012
7	7	1.7621	1.7632	1 1 2	1910.8	1908.3	51.84	51.80	.036
8	8	1.7345	1.7333	2 0 1	1972.0	1974.9	52.73	52.77	-.042
9	9	1.6681	1.6797	0 0 4	2132.1	2102.7	55.00	54.59	.412
10	10	1.4196	1.5213	1 0 4	2944.2	2563.6	65.72	60.84	-1.028
11	11	1.4023	1.4002	2 0 3	3017.0	3026.3	66.63	66.75	-.116
12	12	1.3583	1.3561	2 1 0	3215.6	3226.1	69.09	69.22	-.129

Selected area electron diffraction (SAED) patterns of TEM for Ni doped CdS are shown in figure 2(a)-2(e). The small dimensions of the nanoparticles do not allow the examination of the nanoparticles by conventional selected area electron diffraction. Transmission Electron Microscopy (TEM) bright field images of Nickel (2%,4%,6%,8% and 10%) doped CdS nanoparticles is shown in figure 3(a)-(e). In TEM images the shape of these particles is close to spherical and some aggregation is observed. It is apparent that small particles had aggregated into secondary particles due to their extremely small dimensions and high surface energy [21]. A more careful analysis reveals that the particles are held together by a porous irregular network, some plates have been mostly formed by the aggregation. The average particle size of these nanoparticles is in the range of 19-22nm which is in good agreement with XRD data shown in Table 6.

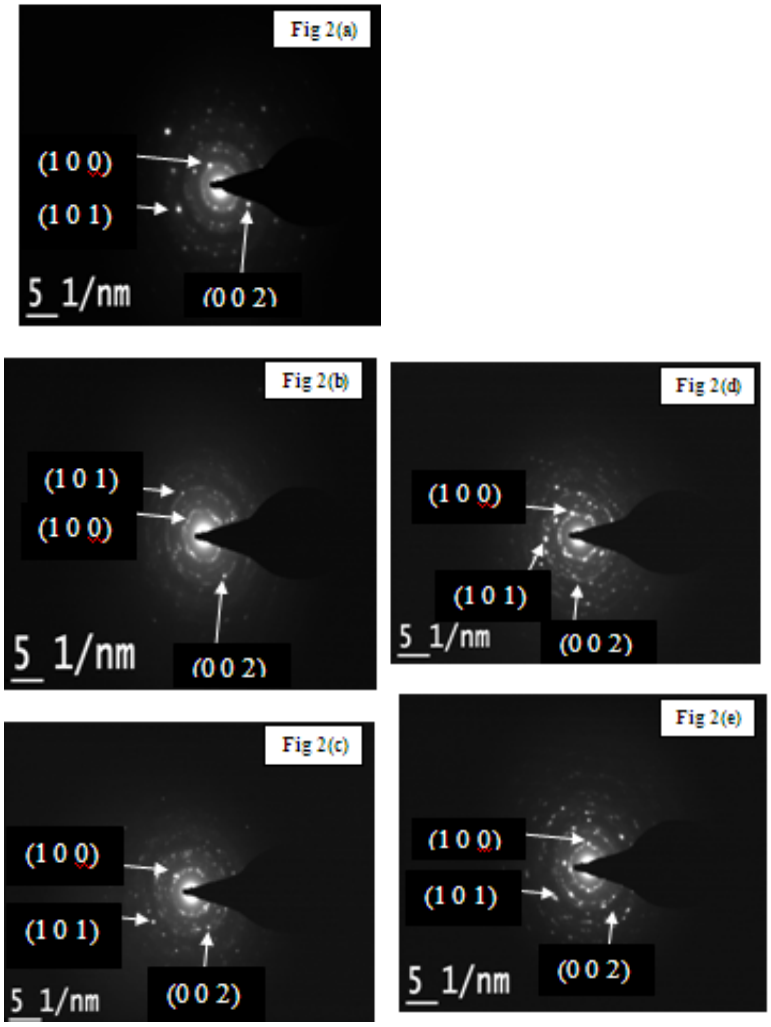

Fig 2(a)-(e) TEM images of Ni (2%, 4%, 6%,8% and 10%) doped CdS sample.

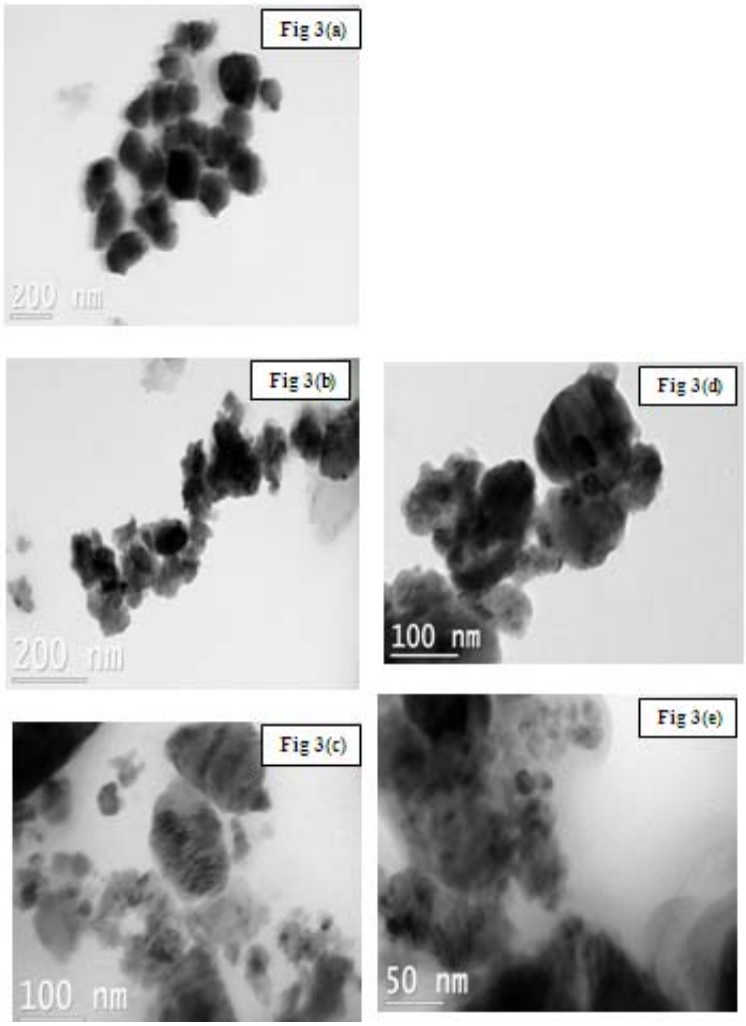

Fig 3(a)-(e) Electron Diffraction(ED) patterns of Ni (2%, 4%, 6%, 8% and 10%) doped CdS sample.

Table 6: Particle size of Ni doped CdS estimated from XRD and TEM data.

S.No	Compound Name	Interplanar Spacing d (nm)		Particle Size D (nm)	
		XRD	TEM	XRD	TEM
1	2 % Ni doped CdS	0.3150	0.3148	21.35	20.16
2	4 % Ni doped CdS	0.3152	0.3151	21.21	19.08
3	6 % Ni doped CdS	0.3147	0.3142	22.32	21.14
4	8 % Ni doped CdS	0.3149	0.3143	22.66	20.86
5	10 % Ni doped CdS	0.3154	0.3149	23.01	22.13

4. Conclusion

Ni doped CdS nanoparticles have been synthesized by aqueous medium through chemical co-precipitation technique. X-ray diffraction measurement confirms the structure

as hexagonal phase having particle size in the range of 21-23 nm.TEM images of Ni doped CdS nanoparticles have a nearly spherical morphology. The small dimensions of the nanoparticles do not allow the examination of a single nanoparticle by conventional selected area electron diffraction (SAED). The average particle size estimated from XRD data are in good agreement with TEM analysis.

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