

Doping-Concentration-Induced Ferromagnetism and photoluminescence emission in CdS: Mn nanoparticles

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ABSTRACT:

Pure and Mn doped CdS semiconductor nanoparticles (NP's) were successfully synthesized by chemical method. The synthesized nanoparticles were subjected to X-ray Diffraction (XRD), EDAX, FTIR, SEM, Photoluminescence and VSM Studies. The structure of CdS and Mn doped CdS from XRD studies is cubic. The excitation wavelength in photoluminescence studies is 340 nm, green and red emissions were observed. The Vibrating sample magnetometer (VSM) studies explores that higher concentration of Mn (7.5%) doped CdS nanoparticles exhibited ferromagnetism.

Key words: Mn doped CdS NP's, Chemical co-precipitation, XRD, FTIR, PL and VSM.

1. Introduction

Shape and size of semiconductor nanoparticles plays an increasingly significant role in achieving the unprecedented optical and electrical properties. Doping, intentional inclusion of impurities into the host semiconductor is also another widely used method to tune the properties of semiconductor nanoparticles. Especially, transition metal doping that can create ferromagnetic property in the host semiconductor has been pursued for several decades to envisage their spintronic application of semiconductors [1-3]. Among all semiconductors, II-VI semiconductors are very popular as host materials to generate room temperature ferromagnetism and attractive photoluminescence properties [4].

CdS is arguably the most important member of functional II-VI semiconductor family due to its wide band gap of 2.4 eV and high luminescence efficiency in the green spectral range. Magnetic elements such as Fe, Cr, Co, Mn, Ni, are used as dopants to impart room temperature ferromagnetism as well as to tune the bandgap and photoluminescence of CdS nanoparticles [5]. Mn has been the most extensively studied dopant in CdS semiconductor. The Optical and magnetic characteristic in CdS and Mn doped CdS may be due to sp-d exchange interactions. On the other hand, Mn doping could induce defects in CdS, which can give rich photoluminescence and magnetic properties. However, the role of these defects in creating the ferromagnetism is still unclear and is under debate [6-7]. Decreasing of impurities and increase of

ferromagnetism with Mn concentration in CdS nanowires was reported by Murali et al. [8]. Systematic investigations is to be required to understand the room temperature ferromagnetism in Mn doped CdS nanoparticles. Several synthesis methods including sol-gel method [9], sonochemical method [10], hydrothermal method [11-12], solvothermal method [13], chemical co-precipitation method [14], reverse micelles method, etc., have been adopted to prepare Mn doped CdS nanoparticles. The role of Mn dopant concentration on the structural, optical and magnetic properties of CdS nanoparticles is explored and results are noticed.

2. Experimental details:

2.1 Materials Used:

The chemicals utilized for this work are cadmium acetate dehydrate [$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] (99%, Sigma Aldrich), Manganese acetate tetra hydrate [$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$] (98.5%, Fisher Scientific) and Sodium Sulphide [Na_2S], 5ml of PEG used as capping agent which will control the agglomeration of particles and deionised water is used as dispersing solvent.

Synthesis of Pure and Mn doped CdS nanoparticles:

In this experiment all the reagents used were analytically pure and used without further purification. Pure and Mn doped CdS nanoparticles are prepared by chemical co-precipitation method using their acetate salts at room temperature. 0.2M aqueous solution of Cadmium acetate dehydrate [$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] and 0.2M aqueous solution of Manganese acetate tetra hydrate [$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$] were mixed together with 50ml of deionised water by stirring for 20 minutes. 0.2M aqueous solution of sodium sulphide prepared separately and taken into a burette then this solution added drop by drop to the above solution and stirred for 20 minutes. After that 5ml of PEG was added and continuously stirred for 7 hours till fine precipitate of yellowish Mn doped CdS Nanoparticles were formed. Then the precipitate was filtered separately and washed several times in deionised water to remove the impurities and dried at 70°C in an oven. Then the dried precipitate were grinded for 30 minutes. After that the powder is kept in the furnace where the temperature was maintained at

70°C for 10 hours and then slowly quenched to room temperature [15]. So that the pure CdS / Mn doped CdS nanoparticles were synthesized.

As synthesized samples were subjected to XRD, SEM, EDAX, FTIR, Photoluminescence and magnetic studies.

3. Results and Discussion

3.1 Elemental analysis:

Energy Dispersive X-Ray analysis (EDAX) is a tool utilized for chemical composition analysis. Fig.1 shows the EDAX Spectra of pure CdS and Mn doped CdS (2.5%, 5%, 7.5%) nanoparticles which confirmed that the other impurities or contaminants were not present in the samples. It was noticed that the elements Cd, S and Mn concentrations were nearly in stoichiometric from EDAX spectrum [16].

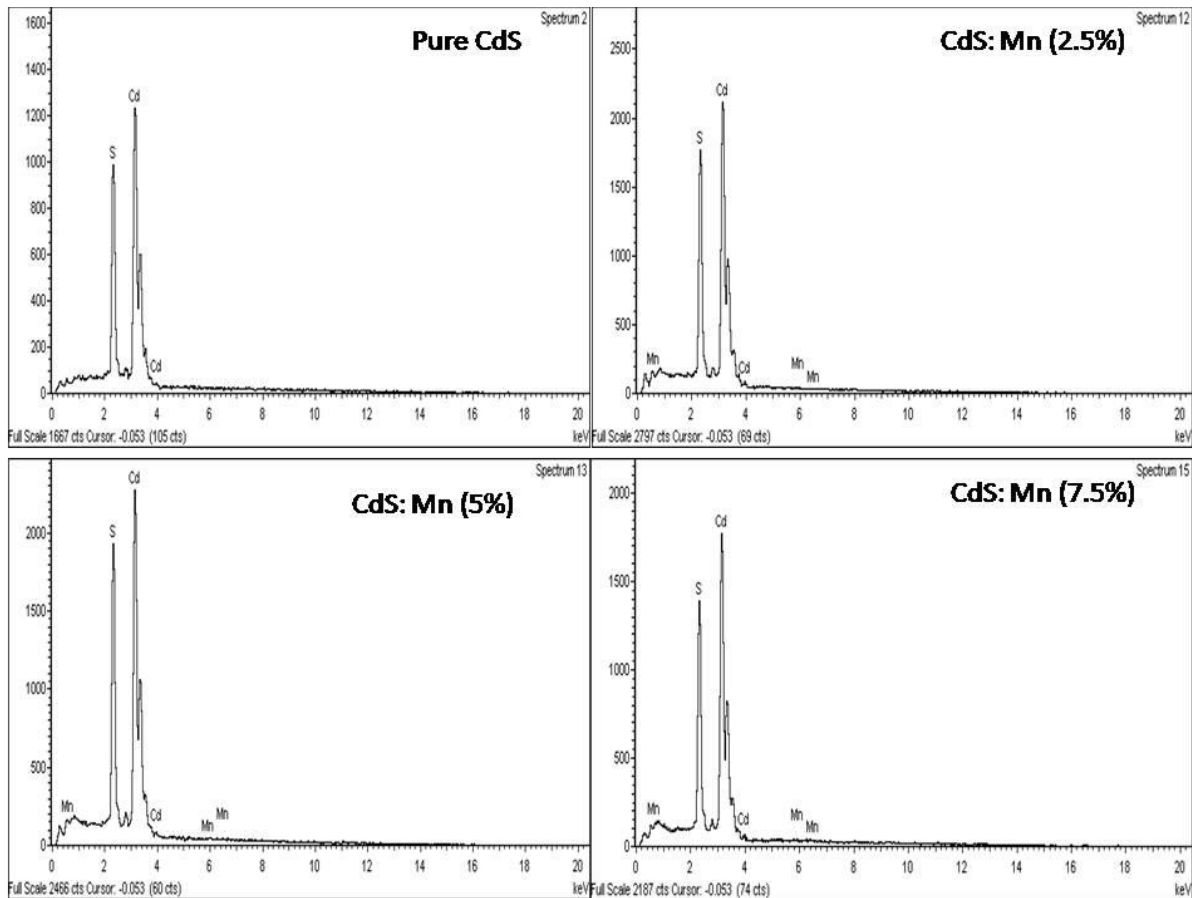


Fig.1 EDAX spectra of Pure and Mn doped Cd S nanoparticles.

3.2 Structural Analysis:

The XRD patterns of CdS and Mn doped CdS (2.5%, 5%, 7.5%) nanoparticles were shown in figure 2. For all four samples the peaks were observed at (1 1 1), (2 2 0) and (3 1 1) which corresponds to cubic structure and no other peaks were noticed.

For all concentrations the lattice parameters were calculated for (1 1 1) by using the equation [16].

$$a = d \sqrt{h^2 + k^2 + l^2}$$

The average grain size (D) was calculated from the Debye Scherer's relation [17]

$$D = \frac{0.94 \lambda}{\beta \cos \theta}$$

Where λ is the wavelength of Cu- K_{α} line (1.54 Å), D is the average particle size.

θ is the diffraction angle and β is the XRD peak's full width at half maximum expressed in radians.

Phase transformation was not observed with Mn doping concentration and the diffraction intensity reduced to low, the average grain size was around 2-3 nm.

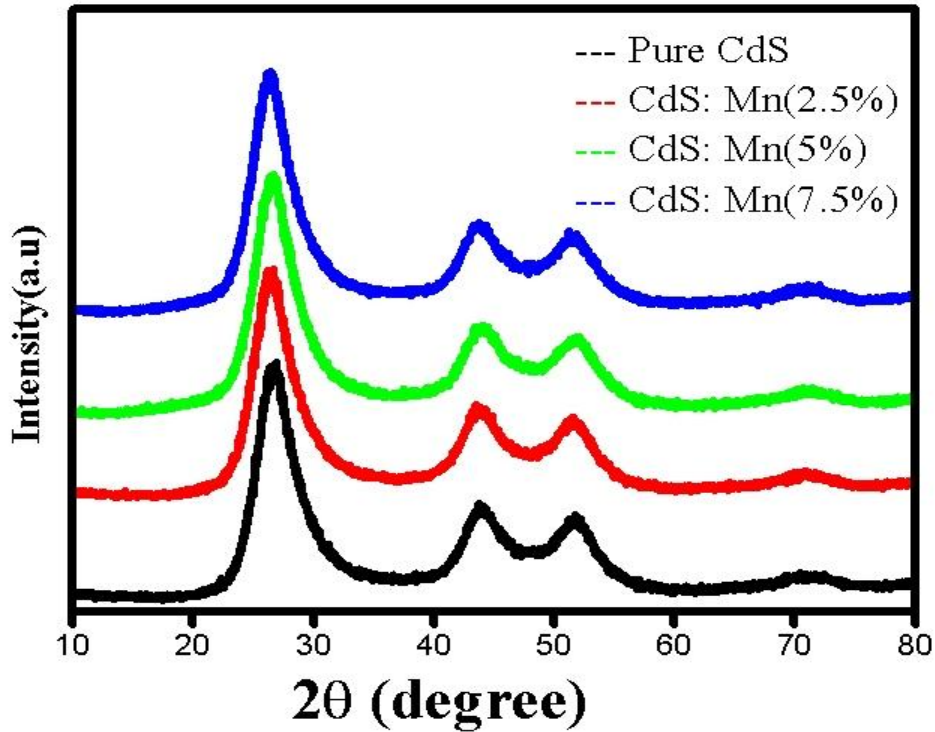


Fig.2 XRD spectrum of Pure and Mn doped Cd S nanoparticles.

Table 1 CdS nanoparticles doped with Mn: Lattice parameters, particle size

Doping Concentration(%)	d-spacing (Å)	Lattice parameter a=b=c(Å)	Particle size from XRD (nm)
0	3.2750	5.8338	2.3
2.5	3.2756	5.7758	2.2
5.0	3.2799	5.8228	2.3
7.5	3.2816	5.7501	2.1

3.3 Morphological studies:

The surface morphology of the pure CdS and Mn doped CdS (2.5%, 5%, 7.5%) nanoparticles was noticed by using the Scanning Electron Microscope (SEM). The SEM images of CdS and

Mn doped CdS nanoparticles capped with PEG are shown in fig. 3. The particles were almost in spherical shape and with increasing of Mn dopant concentration the particle size is decreased and observed agglomeration. For 2.5% the particles are in rock type shape.

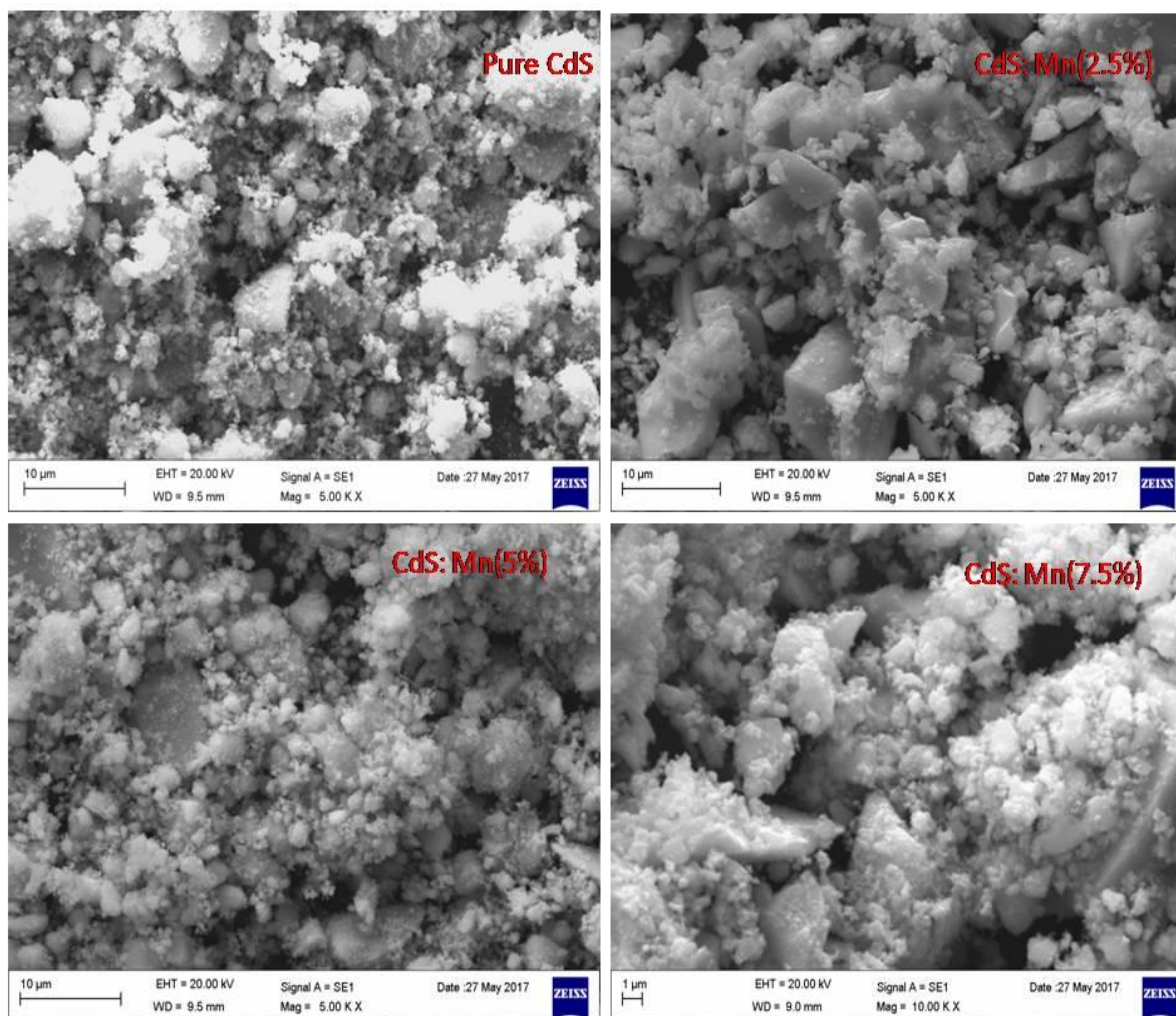


Fig.3 SEM images of Pure and Mn doped CdS nanoparticles.

3.4 FTIR studies:

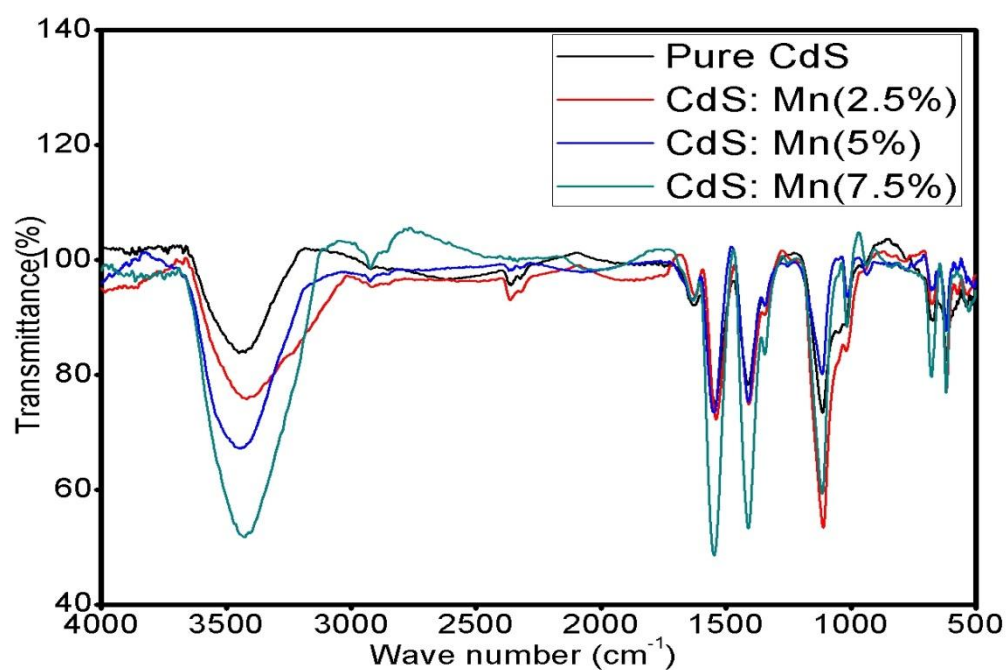


Fig.4 FTIR spectrum of Pure and Mn doped CdS nanoparticles.

The FTIR spectra of Pure CdS and Mn doped CdS(2.5%, 5%, 7.5%) nanoparticles were recorded in the range of 4000 cm^{-1} to 500 cm^{-1} at room temperature. Due to the strong interactions of water molecules with CdS nanoparticles broad and strong peaks at 3425 cm^{-1} and 1626 cm^{-1} were observed due to O-H stretching and O-H bending modes respectively. The peaks at 1412 cm^{-1} corresponds to C-H stretching mode vibration. The narrow peaks at 619 cm^{-1} were attributed to CdS bonding with oxygen from the hydroxyl group of PEG chain [16].

3.5 Photoluminescence studies:

Photoluminescence studies for CdS and Mn doped CdS nanoparticles were carried out at excitation wavelength of 340 nm (2.7 eV). For CdS and Mn doped CdS nanoparticles two emissions were observed at 494nm and 620nm. The emission at 494nm may be due to shifting of electrons from donor levels to valence band [18-19] and red emission can be attributed to sulphur ion vacancies. The intensity increase in Mn doped CdS nanoparticles may be attributed decrease of particle size.

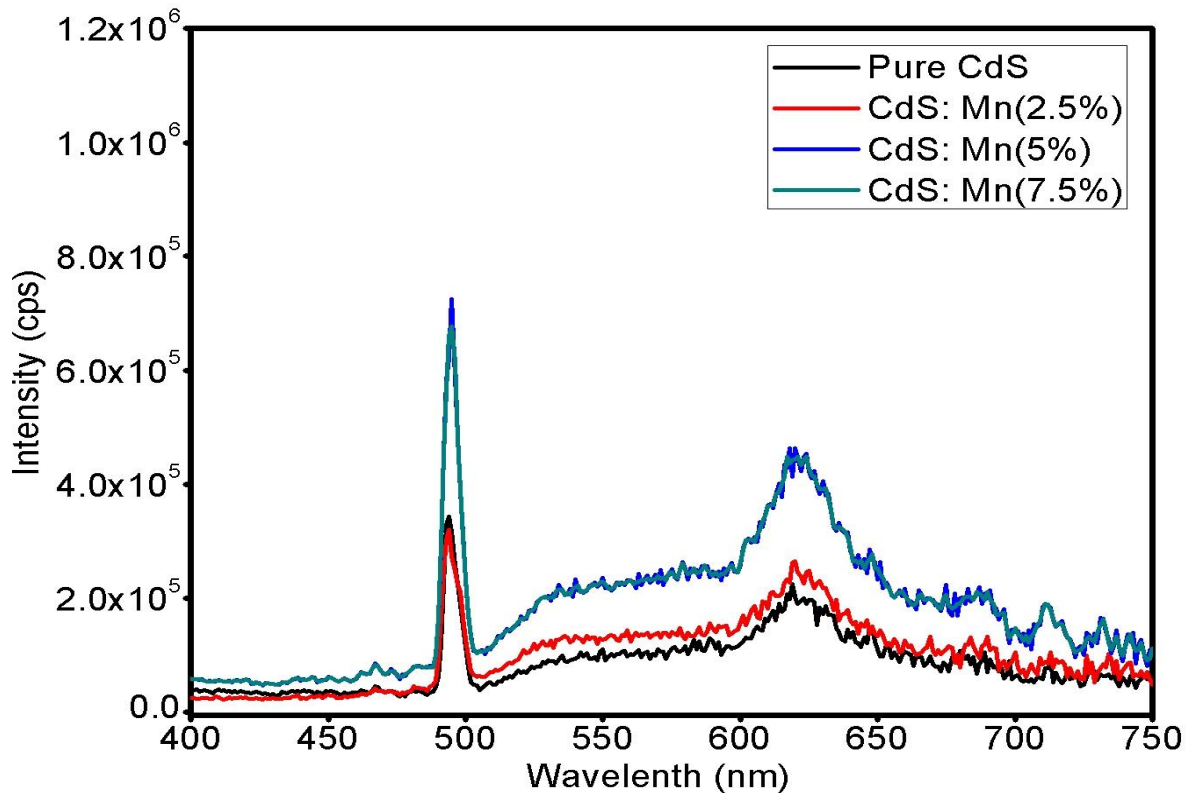


Fig.5 Photoluminescence emission spectra of Pure and Mn doped CdS nanoparticles.

3.6 Magnetic studies:

The different hysteresis magnetization loops were recorded by using vibrating sample magnetometer (VSM). From fig.6 the hysteresis magnetization loops less superimposed on a linear diamagnetic contribution from the glass sample holder. As prepared samples of Pure CdS and Mn doped CdS (2.5%, 5%, 7.5%) nanoparticles exhibit the ferromagnetic nature. The ferromagnetism was

enhanced sharply with increasing the Mn^{2+} concentration in CdS nanoparticles [20-21]. At the level of lower concentration of Mn(2.5% and 5%) doped CdS nanoparticles, the magnetic moments were not considerable for the formation of ferromagnetism hysteresis loop due to the less orientation of the free ions in magnetization direction. Further for concentration of Mn (7.5%) in CdS nanoparticles highly oriented ferromagnetism hysteresis loop is observed.

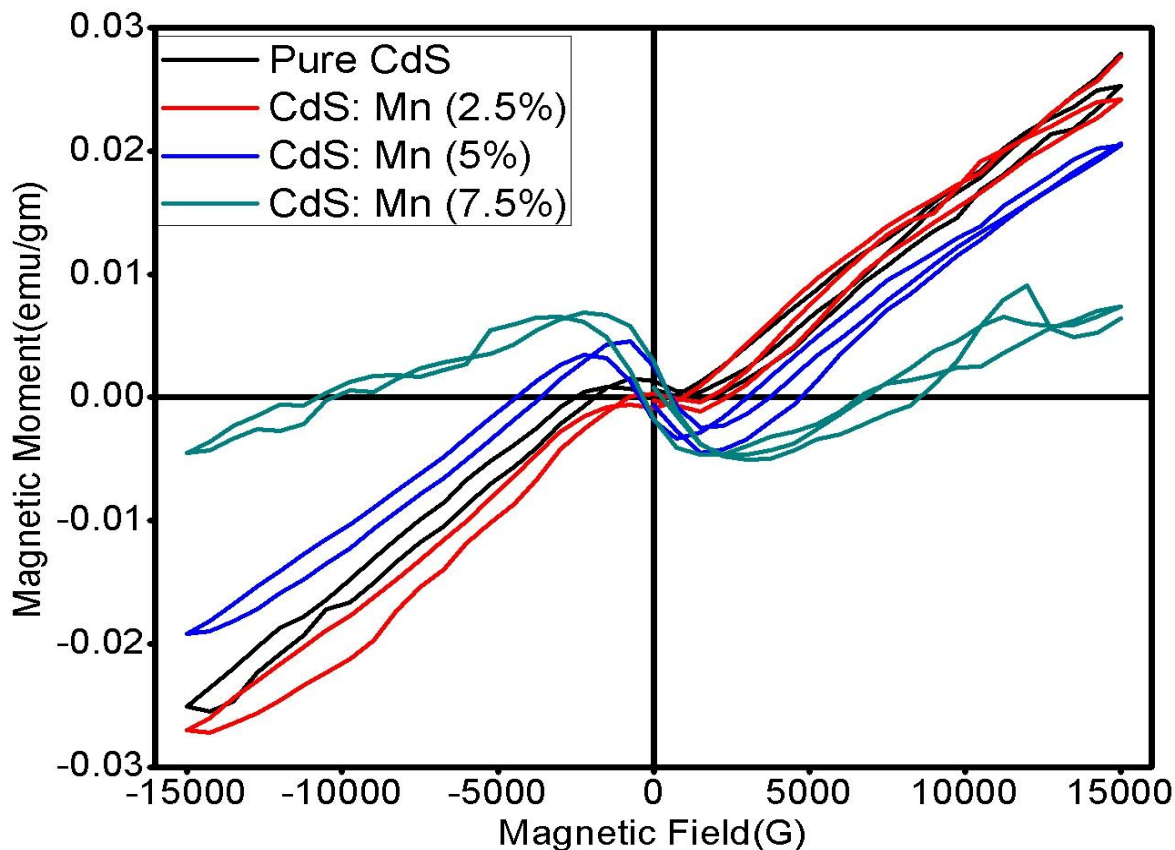


Fig.6 Room temperature M-H behaviour of Pure and Mn doped Cd S nanoparticles.

Conclusions:

CdS and Mn doped CdS nanoparticles were synthesised by using chemical method. The elemental composition analysis revealed the presence of Mn in CdS nanoparticles. The FTIR spectra indicates the presence of capping agent only on the surface of the CdS nanoparticles. XRD studies revealed the cubic structure with single phase without any other impurity phases and particle size was around 2-3nm. From photoluminescence studies strong green and weak red emission bands were noticed for pure and Mn doped CdS nanoparticles. The ferromagnetic nature increased with Mn concentration. CdS and Mn doped CdS nanoparticles has many explored applications.

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