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STRUCTURAL, OPTICAL AND MAGNETIC PROPERTIES OF Cr-DOPED CdSe NANOPARTICLES

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Cr-doped CdSe nanoparticles have been synthesized by solvothermal technique. The effect of doping on structural, morphological, optical and magnetic properties has been investigated. According to the X-ray diffraction (XRD) study, with the increases in Cr-doping concentration in CdSe, the lattice contraction takes place and the structure gets strained whereas the morphological study shows that with increase in Cr-doping particle size decreases. UV-Vis spectroscopy clearly shows blue-shift in the optical band-gap. Pure CdSe nanoparticles are diamagnetic in nature, but, however, with increases in Cr-content (0 - 5 %) in CdSe, they exhibit ferromagnetic behaviour. These synthesised nanoparticles are dilute magnetic semiconductors and are very promising candidates for 'Spintronic' device applications.

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1. Introduction

II-VI semiconductors doped with transition metals, called dilute magnetic semiconductors (DMSs), have attracted the great attention from scientific community due to their potential applications in spin based-devices such as in spin-electronics and spin-photonics [1]. However, to realize a practical implication of spin-based devices, DMSs must exhibit room temperature ferromagnetism [4]. CdSe is one of the most important II–VI semiconductor materials, and, has elite physical properties such as direct band gap of 1.74 eV and electron mobility of 450–900 cm ^{2}/Vs [5-6]. A number of reports on DMSs, with conflicting results - both experimentally as well as theoretically on the observation of room temperature ferromagnetism - have been reported [1-4]. It is theoretically predicted that Cr-doped II-VI semiconductors can show room temperature ferromagnetism [7-9]. The experimental results for (Zn, Cr) Te [7], (Cd, Cr) S [8], (Cd, Mn) Te [9], have further support these theoretical predictions. The exact cause of magnetism in DMSs is still a challenge in scientific community. The present work reports for the first time the room temperature magnetic study in Cr-doped CdSe nanoparticles prepared by solvothermal technique.

2. Experimental detail

Synthesis of Cr-doped CdSe nanoparticles

The chemicals and reagents used were of analytical grade and used without further purification. The synthesis of Cr-doped CdSe nanoparticles has been carried out using solvothermal technique. In the typical synthesis, equimolar concentrations of $CdCl_2.H_2O$ and Se are added in ethylenediamine. The above solution was then transferred to 50 ml autoclave with Teflon liner, and the autoclave was put in an oven at 160^{o}C for 30 hour. The so-obtained product was washed several times with distilled water and ethanol, and finally dried at ambient conditions.

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Characterization

The crystallographic studies of Cr-doped CdSe nanoparticles have been carried out using X-ray diffractometer by PANalytical X'PertPRO MRD with Cu-Kα (λ = 1.54060 Å) radiation operated at 45 kV and 40 mA. The high intense beam was focused over a small area of the sample, and gonio scan was recorded for 2θ values from 10 to 90º. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were carried out for morphological study. The transmission electron microscopy (TEM) measurements were taken with a Hitachi H-7500 system operating at 110 kV. For TEM study, the powder samples was dispersed in ethanol and then one drop of this solution was taken on Cu grid to view the images. For SEM study, the cleaned and dried samples were mounted using a double adhesive carbon tape on an especially designed aluminium stub coated with a layer of gold–palladium alloy using (JEOL, FINE SPUTTER JFC-1100) sputter coating unit and viewed under SEM (JEOL, JSM-6510LV) at 25 kV accelerating voltage. The quantitative elemental composition analysis was carried out by energy dispersive X-ray spectroscopy (EDAX) system attached with SEM of OXFORD analytical. For the optical study, a small amount of dry powder of synthesized nanoparticles is dispersed in ethanol. The UV–Vis absorption spectra of the samples were recorded to determine the optical band gap, using a Perkin-Elmer Lambda 45 Spectrophotometer.

3. Results and discussion

Structural and phase analysis

XRD patterns of pure and Cr-doped CdSe nanoparticles are shown in figure 1. All the peaks are indexed and found to be well matched to wurtzite structure of CdSe having hexagonal phase with lattice parameters a = 4.299 A^o and c = 7.010 A^o which is in good agreement with the (JCPDS card no. 77-2307). The sharp diffraction peaks confirm the high crystallinity of the synthesised nanoparticles.

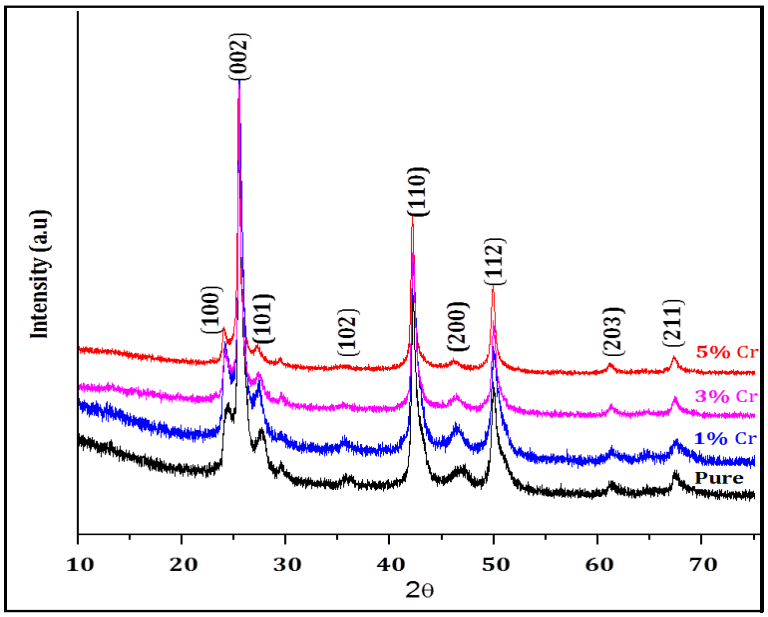

Fig. 1 XRD pattern of pure and Cr-doped CdSe nanoparticles

The crystallite size (D) and the strain (ε) present in the synthesized nanoparticles is calculated by using Debye-Scherer equation:

$$\beta.\cos\theta = \frac{\lambda}{D} + \varepsilon.\sin\theta$$

where λ is the wavelength of x-rays , β is the full width at half maximum (FWHM) and θ is the angle of diffraction. Table 1 shows the calculated crystallite size and lattice strain of pure and Cr-doped CdSe nanoparticles. It is clear from the table 1 that with increase of Cr concentration in CdSe, the average crystallite size decreases. This observed decrease in crystallite size is because of the smaller size of the Cr ions as compared to Cd ions. Also, it is clear from the table 1 that the lattice strain increases because of smaller size of the Cr ions as compared to Cd ions, this results in contraction of lattice; and, due to this, the lattice strain increases. No additional impurities related to Cr has been found, which shows the good dispersivity of Cr in CdSe.

Table 1 Particle size, crystallite size, lattice strain and band gap of pure and Cr-doped CdSe nanoparticles

Cr doping %	Particle size from TEM (nm)	Crystallite size from XRD (nm)	Lattice strain	Band gap (eV)
0	28.57	24.21	0.0035	2.07
1	25.74	23.67	0.0041	2.19
3	20.35	18.95	0.0057	2.25
5	18.75	16.97	0.0071	2.39

Chemical compositional analysis

The chemical compositional analysis of the pure and Cr-doped CdSe nanoparticles has been carried out using EDAX. Figure 2 show the EDAX spectra of pure, 1 %, 3 % and 5% Cr-doped CdSe nanoparticles. It is clear from figure 2 (a) that Cd and Se are in 1:1 atomic % ratio in CdSe, which means they are according to their stoichiometry. This indicates the formation of pure CdSe in stoichiometry. However, around 0.80 %, 2.86 % and5.23 % atomic % of Cr is detected respectively in 1%, 3% and 5 % Cr-doped CdSe nanoparticles. Therefore, the EDAX spectra (Fig. 2) show well agreement with the experimental concentration used to dope CdSe.

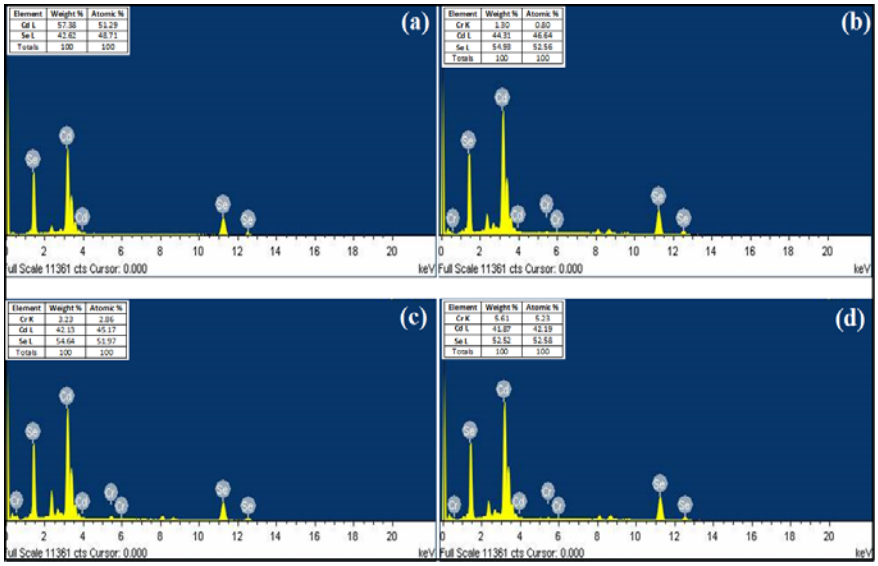

Fig.2 EDAX spectra of (a) pure CdSe (b) 1% (c) 3% and (d) 5% Cr-doped CdSe nanoparticles

Morphological study

TEM analysis

Figure 3 shows the TEM images of pure and Cr-doped CdSe nanoparticles. It is clear from the figure 3 (a) that the average particle size of pure CdSe nanoparticles is around 28.57 nm (Table 1). But with increase in Cr doping concentration from 1 % to 5%, the particles size decreases from 25.74 to 18.75 nm. The observed decrease in the particle size is due to the smaller size of the Cr-ion as compared to that of the Cd ion. It is clear from the figure 3 that pure CdSe nanoparticles are in the aggregated states. However, with increase in the Cr concentration, the CdSe particles get well dispersed and are homogenous at 5 % Cr-doping. Moreover, the TEM results are found to in well-agreement with the XRD results.

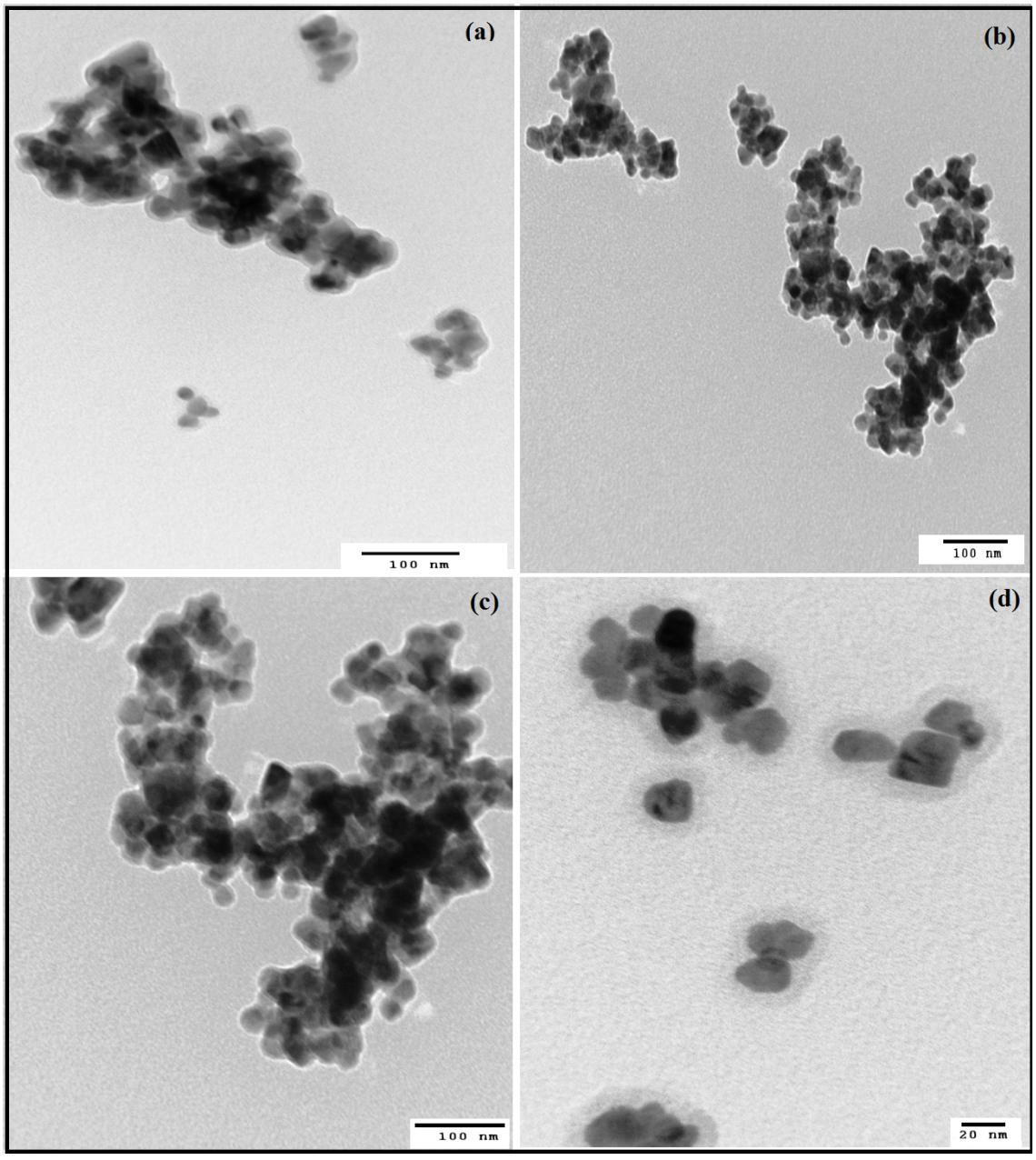

Fig. 3 TEM images of (a) pure CdSe (b) 1% (c) 3% and (d) 5 % Cr-doped CdSe nanoparticles

SEM analysis

Figure 4 show the SEM micrographs of pure and Cr-doped CdSe nanoparticles. It is clear from the figure 4 (a) that the pure CdSe nanoparticles are in the aggregated phase as observed in TEM (Figure 3 (a)). However, with increase in Cr concentration (Figure 4 (b) to (d)), the well-dispersed, smaller in size and more homogeneous CdSe nanoparticles, as compared to the pure ones, have been observed. This might be due to the smaller size of the dopant as compared to Cd; this helps to make the particles well-dispersed, homogeneous and smaller in size (Figure 3 (d)).

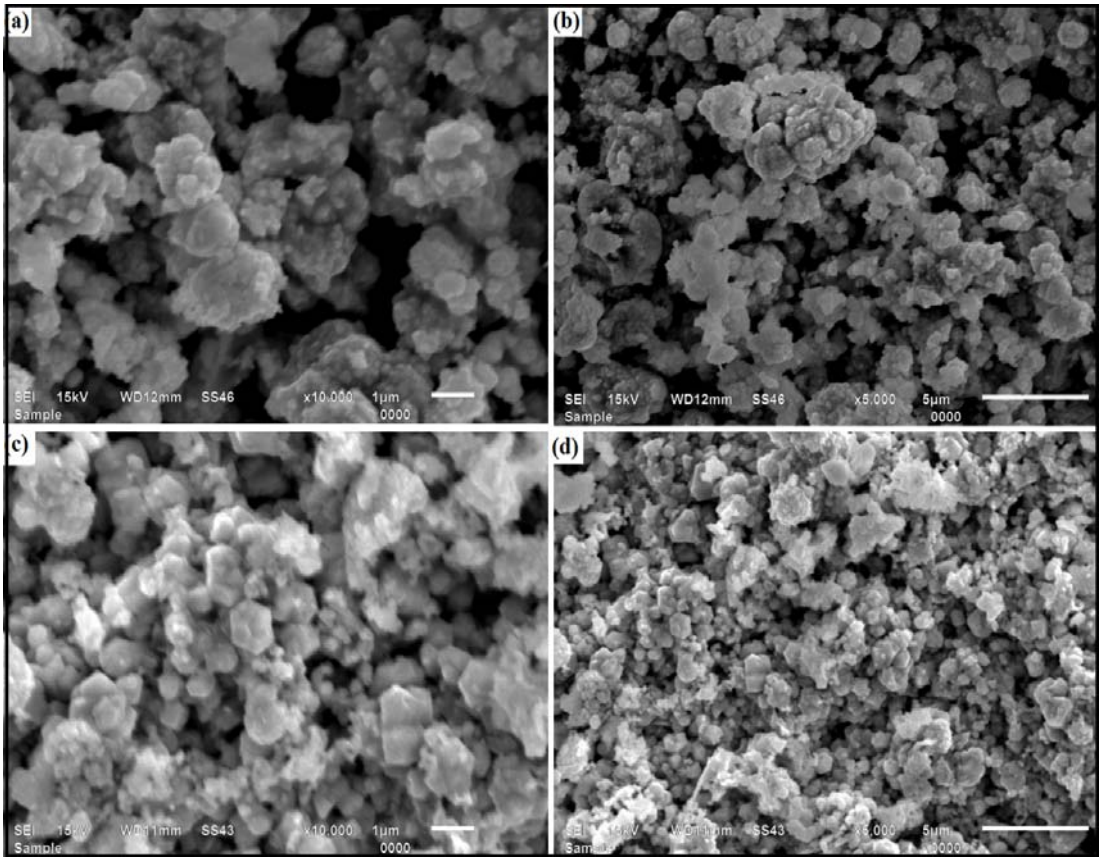

Fig. 4 SEM micrographs of (a) pure CdSe (b) 1% (c) 3% and (d) 5 % Cr-doped CdSe nanoparticles

Optical analysis

Fig. 5 shows the absorption spectra and Tauc's plots of pure and Cr-doped CdSe nanoparticles. The band gaps of pure, 1%, 3% and 5% Cr-doped, calculated from Tauc's relation [10] (figure 5 (b)), have been found to be respectively, 2.07, 2.19, 2.25 and 2.39 eV. The optical band gaps of pure and Cr-doped CdSe nanoparticles have been found in range of 2.07-2.39 eV - clearly higher than its bulk counterpart, i.e., 1.74 eV [6] - showing blue shift of 0.33-0.65 eV. The observed blue-shift in optical band gap can be attributed to two reasons. First, the quantum confinement effect, which is due to localization of electrons and holes in the semiconductor nano-crystallites causing change in the electronic band structure and thereby leading to higher value of optical band gap as compared to the bulk. Second, smaller size of Cr ions (as compared to Cd ions) resulting in the lattice contraction thereby increasing band gap.

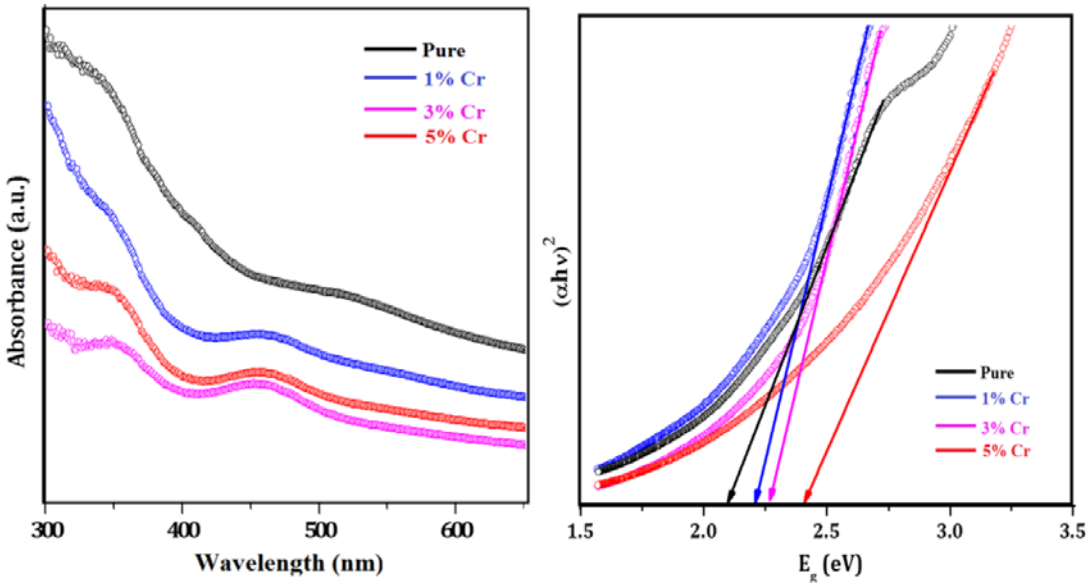

Fig. 5 (a) UV-Vis absorption spectra and (b) band gap calculation from Tauc's relation of pure and Cr-doped CdSe nanoparticles

Magnetic analysis

Figure 6 shows the magnetization versus applied magnetic field (M-H) hysteresis loops of pure and Cr-doped CdSe nanoparticles. It is clear from the figure 6 that the pure and 1% Cr-doped CdSe nanoparticles are diamagnetic in nature. This is due to the fact that the magnetic susceptibility of pure CdSe particles is negative [11]. However, 3% and 5% Cr-doped CdSe nanoparticles show ferromagnetic behaviour. As Cr ions are antiferromagnetic in nature, therefore, even Cr clustering would not induce an extrinsic ferromagnetism [12]. But however, Cr ions acting as magnetic centres possess T*d* site symmetry in host materials, followed by a crystal field and a spin–orbit interaction with Jahn-Teller distortion [13] giving rise to ferromagnetism. There can be two possibilities for doping of Cr ions in the host material – either antiferromagnetism or ferromagnetic super-exchange interaction. Cr ions, despite being antiferromagnetic in nature, favours super-exchange between Cr ions and the host material leading to ferromagnetism. The observed ferromagnetism may also be due to quantum confinement effect.

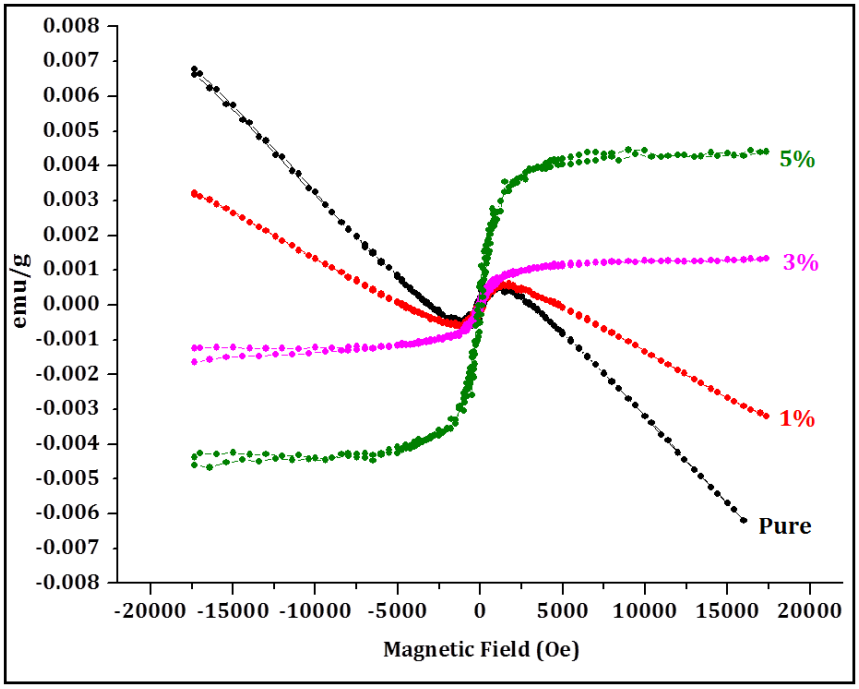

Fig. 6 Magnetization versus magnetic field (M-H) hysteresis loop of pure and Cr-doped CdSe nanoparticles.

4. Conclusions

The synthesis of Cr-doped CdSe nanoparticles has been done by solvothermal technique. The effect of Cr doping on structural, morphological, optical and magnetic properties has been explored. XRD study clearly reveals that Cr-doped CdSe nanoparticles possess wurtzite structure having hexagonal phase. The crystallite-size decreases and lattice strain increases with increase in Cr concentration. Pure CdSe nanoparticles are spherical in nature having particle size 28.87 nm, which further decreases to 18.75 nm with increases in Cr concentration up to 5%. EDAX analysis reveals that pure and doped nanoparticles are in stoichiometric ratio. UV-Vis spectroscopy shows clear blue-shift in energy band-gaps. Pure and 1% Cr-doped CdSe nanoparticles are found to possess diamagnetic behaviour. However, with further increase of Cr-content from 1 to 5%, the doped-CdSe nanoparticles exhibit ferromagnetic behaviour. The so-synthesized dilute magnetic semiconductor nanoparticles are very promising material for the spin-based device application.

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