A Thesis

On

Magnetic behaviour of Co doped CdSe nanoparticles as dilute magnetic semiconductor

Submitted in the partial fulfilment of requirement for the award of the degree of

Master of Science (Physics)

Submitted by

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June 2012

Dedicated

To

My Family

Certificate

This is certify that the report entitled "Magnetic behaviour of Co doped CdSe nanoparticles as diluted magnetic semiconductor" submitted by Ms. Ramandeep Kaur (301004013) of M.Sc (Physics), Thapar University, Patiala was carried out by her under my supervision. She has not submitted this material for credit towards any other degree at Thapar University, Patiala or any other university.

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Abstract

Over the past ten years, the search for compounds combining the properties of semiconductors and ferromagnets has evolved into an important field of materials science. A large portion of the present research is devoted to the II-VI and III-V based dilute magnetic semiconductor. One of today's challenges for the development of future technologies is the realization of devices that control not only the electron charge, as in present electronics, but also its spin, setting the basis for future spintronics. Spintronics represents the concept of the synergetic and multifunctional use of charge and spin dynamics of electrons, aiming to go beyond the semiconductor electronics and magnetic storage technology. The most direct method to induce spin-polarized electrons into a semiconductor is by introducing appropriate transition-metal or rare-earth dopants producing a dilute magnetic semiconductor (DMS). The DMS are semiconducting materials in which a fraction of the host cations can be substitutionally replaced by magnetic ions. These DMS are the building blocks of the future "Spintronics" devices.

Undoped and Co-doped CdSe dilute magnetic semiconductors have been synthesized by solvothermal technique in which SDS (sodium doceyl sulphate) is used as capping agent for stability. The structural and phase analysis is done with the help of X-ray diffraction (XRD). UV-Visible absorption spectroscopy is used for the study of the optical properties. The morphology of the synthesized nanoparticles is analyzed by transmission electron microscope. Superconducting quantum interference device (SQUID) is used for the magnetic study and Energy dispersive X-ray spectroscopy (EDX) is used for the elemental analysis. The pure CdSe nanoparticles show diamagnetic behavior and they are non uniform but Co doped CdSe nanoparticle shows ferromagnetic behaviour with spherical shape.

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Chapter 1

Introduction

Introduction

The prefix “nano” is began to use by researchers more than thirty years ago, but its use has spread to practically just from last ten years in every field of science and technology. Nanotechnology is the term used to cover the design, construction and utilization of structures with at least one characteristic dimension measured in nanometres. Today it is used as much for fashion as it is for scientific classification and we have reached the point where it is possible to manipulate materials at the molecular level that can be used for particular applications. Such materials can be designed to exhibit significantly improved physical, chemical and biological properties, by controlling shape and size of their constituent particles at the nanoscale. The objects at nanoscale may display physical attributes significantly different from those displayed by either atoms or bulk materials. Ultimately this can lead to new technological opportunities as well as new challenges. [1] Nanotechnology should really be called nanotechnologies: The term broadly refers to such fields as biology, physics or chemistry, any scientific field really, or a combination thereof, that deals with the deliberate and controlled manufacturing of nanostructures. Quantum effects can responsible for the dominating behaviour of matter at the nanoscale. The goal of evolutionary nanotechnology is to improve existing processes, materials and applications by scaling down into the nano realm and ultimately fully exploit the unique quantum and surface phenomena that matter exhibits at the nanoscale.

Physicists are trying to exploit the 'spin' of the electron along with its charge to create a notable new generation of ‘spintronic ' devices. Instead of solely relying on the electron’s negative charge to manipulate electron motion or to store information, spintronic devices would further rely on the electron’s spin degree of freedom. The manipulation of the spin of the electrons along with the charge will open up a faster and more efficient mode of information storage and transfer for quantum computation and communication [2]. The discovery of giant magnetoresistance (GMR) in multilayer of magnetic and nonmagnetic bilayers and the theoretical model of Data-Das field-effect transistor (FET) first stimulated the scientific community to use the spin degree of freedom of electron along with its charge in electronics and born a multidisciplinary field of research, namely, spintronics. The past 60 years after the discovery of transistor action in germanium observed at Bell Laboratories in1947 have the witness of revolution in semiconductor-based electronics mainly because of adding holes +ve charge degree of freedom of carriers in semiconductor along with electrons −ve charge. Adding further spin degree of freedom in conventional electronics is expected to be enhanced the functionality of new electronic devices such as non volatile memory, low-power consumption, high speed and large integration density compared with the conventional semiconductor devices. Two distinct approaches are clearly observed in spintronics. One is based on the GMR effect in magnetoresistive (MR) elements, which is composed of two ferromagnetic layers separated by a nonmagnetic metal or insulator and already applied successfully in practical devices such as read head, spin valve, magnetic random access memory and closed to realize magneto-logic gates such as AND,NAND, OR, and NOR. Another approach is based on the spin injection into semiconductor either through the interface of ferromagnetic/semiconductor heterostructures or ferromagnetic ions doped into the semiconductor dilute magnetic semiconductor DMS [3].

1.1 Dilute magnetic Semiconductor

The material joining both the characteristics of semiconductor as well as magnetic material known as Dilute Magnetic Semiconductor or semimagnetic semiconductor. The DMS are semiconducting materials in which a fraction of the host cations can be substitutionally replaced by magnetic ions (Fe, Co, Ni etc) or appropriate rare earth elements [4] as shown in Fig1.1.

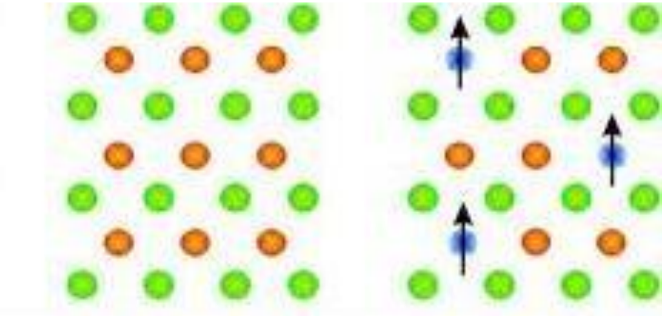

Fig.1.1. Semiconductor host (parrot) atoms with magnetic impurity in (blue)

There is a wide class of semiconducting materials which is characterised by the random substitution of a fraction of the original atoms by magnetic atoms. The materials are commonly known as semimagnetic semiconductors (SMSC) or diluted magnetic semiconductors (DMS). The most common DMS are II-VI compounds (like CdTe, ZnSe, CdSe, CdS, etc.), with transition metal ions (e.g. Mn, Fe or Co) substituting their original cations. There are also materials based on IV-VI (e.g. PbTe, SnTe) and recently III-V (e.g. GaAs, InSb) crystals. On the other hand, rare earth elements (e.g. Eu, Gd, Er) are also used as magnetic atoms in DMS. The most distinctive feature of dilute magnetic semiconductors (DMSs) is the strong exchange interaction (s, p–d exchange interaction) between the d spins of the magnetic transition metal ions and the sp carriers of the host semiconducting material. Both the structure and the electronic properties of the host crystals are well known means that they are perfect for studying the basic mechanisms of the magnetic interactions, coupling the spins of the band carriers and the localized spins of magnetic ions. The coupling between the localized moments results in the existence of different magnetic phases (such as paramagnets, spin glasses and antiferromagnets). By using these interactions, controlling electrical and optical characteristics of the semiconductor by magnetic field becomes possible. This interaction also enables one to change the magnetic characteristics of the material by electric and optical means. Moreover, it is understood that the appearance of the ferromagnetism observed in some DMS, such as $Ga_{1-x}Mn_xAs$, is due to this s, p–d exchange interaction. Therefore the confirmation of the s, p–d exchange interaction is the most important task to be carried out when new materials intended to be DMS are synthesized. Characterization of the s, p–d exchange interaction has been a main topic for the DMS. The wide variety of both host crystals and magnetic atoms provides materials which range from wide gap to zero gap semiconductors, and which reveal many different types of magnetic interaction. Several of the properties of these materials like energy gap, effective mass may be tuned by changing the concentration of the magnetic ions. The various semiconductors doped with magnetic impurities (DMS) are given below [5, 6, 7]

III-V	II-VI	IV-VI	IV	Oxides	Others
GaMnAs GaMnN GaMnP InMnAs	ZnMnSe ZnCrTe ZnCrSe CdMnTe CdMnSe	PbMnTe PbSnMnTe	GeMn SiMnC	ZnO:Co ZnO:Co TiO_2:Co SnO_2:Co HfO_2:Co Cu_2O:Co	$CdGeMnP_2$ $ZnGeMnP_2$ ZnSnMnAs

There are two major criteria for selecting the most promising materials for semiconductor spintronics.

1. The ferromagnetism should be retained to practical temperatures (i.e. >300k)
2. It would be a major advantage if there were already an existing technology base for the material in other applications.

1.1a Properties of DMSs

The semiconducting properties of DMS, such as the energy gap, the effective mass etc. can be varied in a controlled fashion by varying the composition, e.g., $Cd_{1-x}Mn_xSe$.

The presence of magnetic ions in the DMS lattice leads to spin-spin exchange interaction between the localized magnetic moments and the band electrons, resulting in new effects such as

- Zeeman splitting
- The Spin glass behaviour
- Room Temperature Ferromagnetism (RTF)
- Anomaolous Hall effect
- Superparamagnetism

1.2 Cadmium selenide (CdSe)

Cadmium selenide (CdSe) is a solid, binary compound of cadmium and selenium. Cadmium selenide is a semiconducting material, but has yet to find many applications.

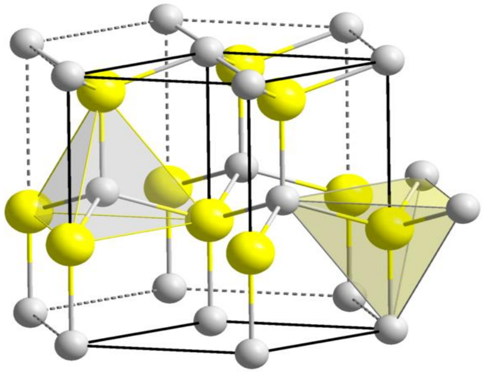

Fig.1.2a. Wurtzite(Hexagonal)

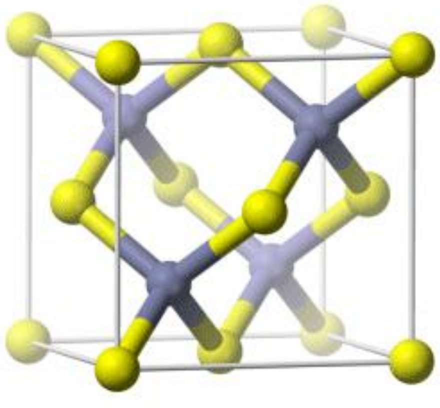

Fig.1.2b. Wurtzite (Cubic)

This material is transparent to infra-red (IR) light. Two crystalline forms of CdSe are known: wurtzite (hexagonal) and rock-salt (cubic) shown in figure1.2. These structures only differ in the stacking sequence of the CdSe hexagonally packed layers.

The Wurtzite structure has an ABABAB stacking sequence, while the rock-salt structure has an ABCABC stacking sequence. The sphalerite CdSe structure is unstable and converts to the wurtzite form upon moderate heating. The transition starts at about 130 °C, and at 700 °C it completes within a day. The rock-salt structure is only observed under high pressure [8].

Much current research has focused on the nanoparticles of cadmium selenide. Researchers are concentrating on developing controlled syntheses of CdSe nanoparticles. In addition to synthesis, scientists are working to understand the properties of cadmium selenide, as well as apply these materials in useful ways.

The production of cadmium selenide has been carried out in two different ways

1. The preparation of bulk crystalline CdSe is done by the High-Pressure Vertical Bridgman method or High-Pressure Vertical Zone Melting.

Cadmium selenide in its wurtzite crystal structure is an important II-VI semiconductor.

Property /material	Zinc Blend lattice parameter at 300K	Zinc Blend density at 300K	Wurzite lattice parameters at 300K	Wurzite lattice density at 300K	Phase stable at 300K	Refractive index	Energy gap E_g at 300K Wurzite
CdSe	0.608nm	5.655 cm^{-3}	a_0=0.430 nm c_0=0.6749nm	5.819 cm^{-3}	Wurzite	2.5	1.714ev

2. Methods for the production of CdSe nanoparticles have been developed:--

- ✓ Synthesis in structured media
- ✓ High temperature pyrolysis

- ✓ Sonochemical
- ✓ Radiolytic

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Chapter 2

Literature Review

The dilute magnetic semiconductor (DMS) is the building blocks for the "Spintronics" device applications. The study of ferromagnetic and semiconducting properties of $CrBr_3$ was started in 1960s but these properties were found at very low Curie temperature i.e. about 37 K. Most of the past work on DMS has focussed on various materials like EuO, MnAs, MnSb, $CdCr_2S_4$, Sr_2FeMnO_6, with improvement in Curie temperature. [1]. The considerable attention has paid to II–VI compounds such as CdTe, ZnSe, CdSe, CdS doped with Mn. But these DMS are less attractive for applications because of their low Curie temperature [2]. Instead of II-VI, the III–V DMS semiconductors widely used for high speed electronic and optoelectronic devices. Because of exceptional optical and magnetic properties, rare earth and transition metal doped II-VI materials become most promising in the field of current research. By doping of these nanostructures with rare-earth and transition-metal ions optical properties can be controlled by the magnetic field and vice-versa.

Several researchers are working to find suitable materials as DMSs. The huge part of their work has been done on ferromagnetic metal doped II-VI semiconductor nanoparticles (NPs). The most promising DMS materials are CdSe [3], CdS [4], ZnSe [5], ZnS [6], CdTe [7], ZnTe [8] doped with transition or rare earth metal ions. But the broad range of research has been focussed on CdSe NPs as a host material, and its DMS behaviour can be explored by doping with suitable magnetic ions [3]. The CdSe nanoparticles being a direct band gap semiconductor and they shows very interesting properties such as energy band gap tuning, optical, electronic, and electrical properties just by varying its dimensions and addition of suitable dopant.

Hanif et al. [9] in 2002 reported the magnetic ordering in Co-doped CdSe DMS quantum dots. This paper discussed the structural and magnetic properties of Co-doped CdSe quantum dots. In this system stronger sp-d orbital mixing has been observed as compare to their bulk counterpart which leads to enhanced superexchange interaction in this system.

Meulenberg et al. [10] in 2004 reported the electronic and chemical structure of Cu doped CdSe nanocrystals by employing X-ray absorption near edge spectroscopy (XANES). The PL band shifts to lower energy as well as it is quenched by increasing the doping concentration. The Se vacancies in the low doped CdSe NPs may cause large increase in the defect. The X-ray spectroscopy can be used to identify the presence of Cu in the CdSe nanoparticle with +1 oxidation state which introduces charge imbalances in the NPs.

Archer et al. [11] in 2007 reported the sp-d exchange interactions which are responsible for magnetism in Mn^{2+} and Co^{2+} doped CdSe quantum dots. The magnetic circular dichroism spectroscopy (MCD) is used to express strong sp-d exchange interactions in $Mn2^{+}$ and Co^{2+} doped CdSe QDs. The magnitudes of the excitonic Zeeman splittings, for both Mn2+: CdSe and Co2+: CdSe QDs can be calculated by using MCD microscopy which is greater than the undoped CdSe nanocrystals under the same conditions. This study demonstrates that transition metal doped CdSe QDs are attractive materials for studying spin effects and relevant to spin based information processing.

Singh et al. [12] in 2008 reported the room temperature ferromagnetism (RTFM) in pure and copper doped CdSe nanoparticles. It is found that at lower doping concentration of copper, the saturation magnetization value increases but it decreases consistently with high concentration. Cu metal and all its secondary phases are not ferromagnetic and bulk CdSe is diamagnetic in nature which should not show a magnetic hysteresis loop at room temperature. The intrinsic defect in CdSe nanocrystallites is probably responsible for the observed room temperature ferromagnetic order, also the interaction of the capping agent with the nanoparticles surface provide necessary magnetic ordering.

M.S. Seehra et al. [13] in 2008 reported the observation of RTFM in CdSe quantum dots (QD) capped with TOPO (tri-n-octylphosphine oxide). XANES (X-ray absorption near-edge structure) and EXAFS (extended X-ray absorption fine structure) spectra of TOPO-capped CdSe QDs is used to measure the charge transfer from Cd to TOPO. The electronic structure of samples represented by the XANES spectra , whereas EXAFS tells about local structure of the absorbing atom. As size of QDs decreases there is an increase in the number of unoccupied states and it further increases charge loss in the occupied states of Cd ion. The size of QDs also affects the ordered local structure, as size goes on decreasing there is more disorder in local structure. The charge redistribution with the capping agent TOPO is responsible for the increment in the d-hole population of the Cd 4d band with reduction in size of the CdSe QDs. The saturation magnetization is inversely proportional to size D.

Meulenberg et al. [14] in 2008 reported the evidence for ligand-induced paramagnetism in CdSe QDs. They found that the induced paramagnetism in CdSe QDs is because of manipulation of the surface chemistry or variation of the end-group functionality of the passivating layer. Further the paramagnetism in CdSe QDs depends on the type of capping agent such as CdSe-HDA (hexadecylamine), CdSe-TOPO (trioctylphosphine), and CdSe-DDN (dodecanitrile).

Singh et al. [15] in 2009 presented the optical and magnetic properties of Fe substituted CdSe nanoparticles. The presence of Fe^{+3} oxidation state in CdSe is discussed in the Moessbauer and EPR spectra. The thiol capped CdSe NPs shows room temperature ferromagnetic behaviour. The doping concentration of Fe in CdSe NPs which is limit for saturation magnetisation is 8.58%, because further increase in Fe concentration changes its behaviour from ferromagnetic to paramagnetic. The *F*-center exchange mechanism leads to the ferromagnetic coupling, where *F*-center is similar to bound magnetic polaron. , charge imbalance, defects.

Sudaresan et al. [16] in (2009) reported that the room temperature ferromagnetism is a universal characteristic of inorganic nanoparticles. They shows that different types of nanoparticles such as CdS, CdSe, superconductors; CeO_2, TiO_2, Al_2O_3, MgO, nitrides; GaN, chalcogenides; $YBa_2Cu_3O_7$ exhibit ferromagnetism at room temperature.

Sunil kumar et al. [17] in 2012 reported room temperature magnetism in Ni-doped CdSe nanoparticles. CdSe NPs shows diamagnetic behavior as that of bulk CdSe. The localized spin of Ni^{+2} in the lattice is responsible for of paramagnetic behaviour of 3% Ni doped CdSe NPs. By further increasing the concentration of Ni in CdSe NPs ferromagnetic behavior has been observed, it is because of the magnetic exchange between the interacting Ni^{+2} ions occupying the lattice sites in the CdSe NPs. Ni-Ni direct interaction also provides additional magnetism in the system.

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Chapter 3

Objectives

3.1 GAPS IN STUDY

By reviewing literature it has been found that“ The magnetic study of Co doped CdSe nanoparticles at room temperature” is not well explored till now.

3.2 OBJECTIVES

- ✓ Synthesis of pure and Co doped CdSe nanoparticles by chemical route.
- ✓ The synthesized CdSe nanoparticles; structurally characterized by X-ray diffraction (XRD), morphologically by Transmission Electron Microscopy (TEM).
- ✓ UV-Visible spectroscopy is used for the optical study of NPs.
- ✓ The elemental analysis or chemical characterization by Energy Dispersive X-Ray Spectroscopy (EDX)
- ✓ The magnetic study of sample by Superconducting quantum interference device (SQUID)

3.3 METHODOLOGY

To achieve the objectives follow the steps as given below:

- ➢ **Synthesis of Co doped CdSe nanoparticles:** will be carried out using solvothermal technique.
- ➢ **Structural Analysis:** To know about the crystal structure, crystallinity, and phase transformation the XRD will be used.
- ➢ **Morphological Characterization**: TEM can be used to characterize the nanostructure of materials which will give information about the morphology, crystal structure and defects, crystal phases and composition.
- ➢ **Optical analysis:** Absorption, Band gap of synthesized nanoparticles can be determined by UV-Visible spectroscopy.
- ➢ **Magnetic measurements:** The SQUID characterization will be done to know about the magnetic behavior of synthesized materials.

Chapter 4

Experimental and Instrumentation

4.1Synthesis of nanoparticles

Nanostructures can be made in numerous ways. A broad classification divides methods into either those which build from the bottom up, atom by atom, or those which construct from the top down using processes that involve the removal or reformation of atoms to create the desired structure [1]. The two approaches are schematically represented in Figure3.1.

4.1a Bottom-up approach

In this approach atoms, molecules and even nanoparticles themselves can be used as the building blocks for the creation of complex nanostructures; the useful size of the building blocks depends on the properties to be engineered.

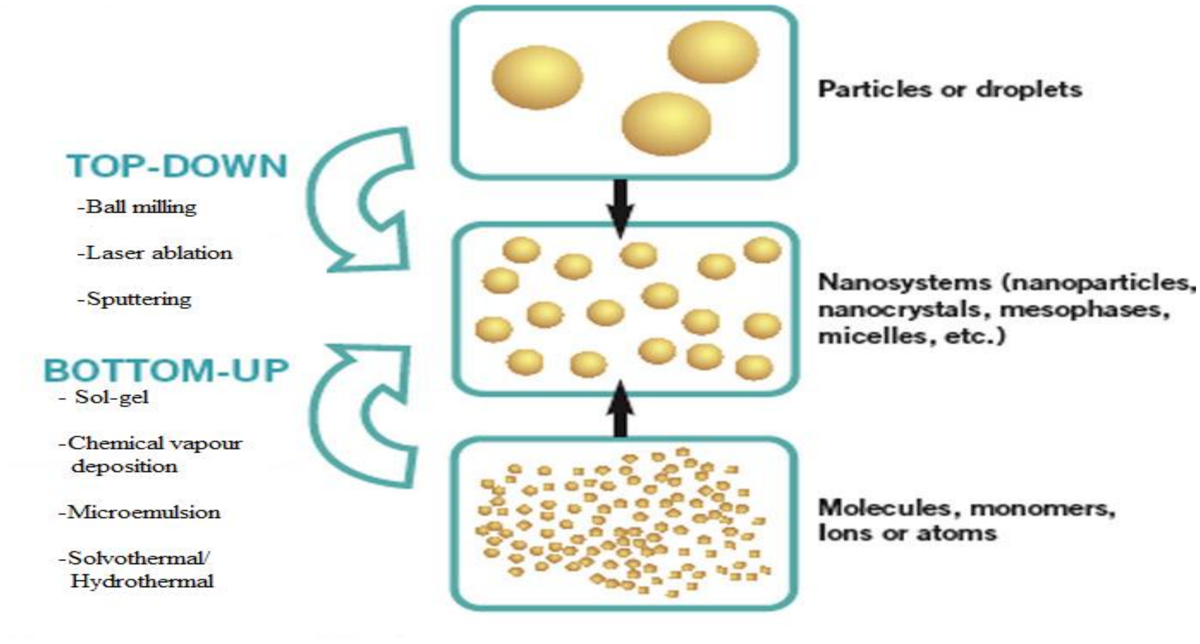

Figure4.1. Systematic of top down and Bottom up approaches

By altering the size of the building blocks, controlling their surface and internal chemistry, and then controlling their organization and assembly, it is possible to engineer properties and functionalities of the overall nanostructures solid or system. These processes follow the highly controlled and complex chemical synthesis procedure.

4.1b Top-down approach

It is inherently simpler and relies either on the removal or division of bulk material, or on the miniaturization of bulk fabrication processes to produce the desired structure with the appropriate properties.

4.1c Solvothermal/Hydrothermal Technique

Solvothermal/Hydrothermal processes can be described as a reaction or a transformation of precursor(s) in presence of a solvent in a close system and at a temperature higher than the boiling temperature of the solvent; Consequently at least autogeneous pressure parameter is involved and the respective chemical properties of the precursor(s) and the solvent such a system can be homogeneous (if the precursors are soluble in the corresponding temperature and pressure conditions) or heterogeneous (if the precursor is partially soluble in such conditions) [2]. Very often in order to improve such solubility an initial high pressure is used. Versus the temperature, the system can be in subcritical and supercritical conditions. The most developed solvent was water due to its presence at the surface of the earth and its specific role in geochemistry. Different objectives have been assigned to hydrothermal processes: (i) to investigate the elaboration of different natural materials in order to improve the knowledge in Earth-Science, (ii) to develop hydrometallurgy for recovering ores,(iii) to synthesize novel materials, very often metastable when the kinetical effects were predominant, (iv) to prepare single crystals of oxides in particular that corresponding to low-temperature structural varieties, (v) to elaborate fine particles as micro- or nanocrystallites. During these last twenty years non-aqueous solvents were developed for preparing in mild conditions oxides or non-oxides materials through solvothermal processes – mainly as fine particles with specific size and shape for different applications.

Solvothermal reactions are governed by different factors:

- the nature of the precursors, in particular their physico-chemical properties (solubility, thermal stability),
- the nature of the solvent (chemical composition, physico-chemical properties solvatation, polarity, viscosity, ability to stabilize some complexes as intermediate steps),
- the thermodynamical properties used during such a process (pressure and temperature).
- pressure and temperature can play an important role, some properties of the solvent such as density, viscosity, changing drastically versus such parameters.

Consequently the diffusion and reactivity of chemical species can be strongly affected. In a general way, solvothermal processes were developed in mild temperature conditions. The main chemical reaction-types involved in solvothermal processes are: hydrolysis, complex-formation, metathesis, oxidation-reduction [3].

4.2 Characterization Techniques

There are various characterization techniques which are used for the determination of elemental composition, structural analysis, morphological analysis, magnetic analysis, identification of crystalline phases and information on crystal defects. . The nanostructures have been characterized by their structural, compositional, morphological, optical and magnetic properties by including the techniques like UV-visible Absorption Spectroscopy, X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), Energy Dispersive X-rays Spectroscopy (EDX) and superconducting quantum interference device (SQUID).

4.2a Ultraviolet-visible spectroscopy

Absorption of light by solution is one of the oldest and still one of the more useful instrumental methods. Ultraviolet-visible spectroscopy (UV-Vis or UV/Vis) shown in figure4.2a refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region (i.e 200nm – 800nm) of the electromagnetic spectrum. In this region of the electromagnetic spectrum, atoms, ions or molecules undergo electronic transitions from ground state to excited state. The absorbed or transmitted light for given material is the characteristic of its chemical structure. A spectrum is a graphical representation of the amount of light absorbed or transmitted by matter as a function of the wavelength.

Figure4.2a UV-visible spectrophotometer (Hewlett-packard 8452a Diode array Spectrophotometer)

Beer-Lambert Law

The Beer-Lambert Law states that:

$$A \alpha C \tag{1}$$

$$\alpha L \tag{2}$$

combining eq.(1) and eq.(2) we have :

$$A = \varepsilon C L$$

also,

$$A = \log_{10} I_0 / I = \varepsilon(\lambda) C L$$

where I_0 is the incident light intensity, A (dimensionless quantity) is the absorbance , L(cm) is the cell path length , C is concentration (moles/liter) of the solution and ε is the molar absorptivity (liter/mole/cm).

The law is only true for monochromatic light, i.e. light of a single wavelength or narrow band of wavelengths, but the physical or chemical state of the substance does not change with concentration. When monochromatic radiation passes through a homogeneous solution in a cuvette, the intensity of the emitted radiation depends upon two factors which are the thickness (l) and the concentration (C) of the solution [4].

Instrumentation

Figure4.2a1 shows the instrumentation and working of the UV-Vis spectroscopy [2]. In this the radiation source (Deuterium lamp – covers the UV – 200-330 nm and Tungsten lamp – covers 330-700 nm) enters the monochromator through the entrance slit. In monochromator beam is collimated, and then strikes the dispersing element at an angle. The beam is split into its component wavelengths by the grating or prism. By moving the dispersing element or the exit slit, radiation of only a particular wavelength leaves the monochromator through the exit slit., The beam splitter sends a separate band to a cell(called a cuvette") containing the sample solution and a reference solution. The detector measures the difference between the transmitted light through the sample (I) vs. the incident light (I_0) and sends this information to the recorder [5].

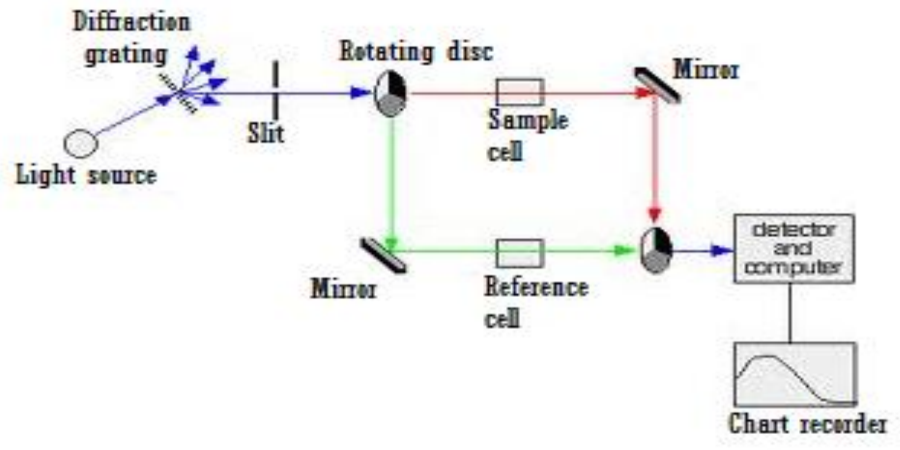

Figure 4.2a1 Principle of UV-VIS Spectroscopy

UV-Visible spectroscopy finds applications in Quantitative determination of solutions of transition metal ions, Quantitative determination of highly conjugated organic compounds, detection of impurities, band gap (Eg).

4.2b X-ray diffraction (XRD)

X-ray diffraction (XRD) shown in figure4.2b is a common non-destructive technique that reveals detailed information about the chemical composition, atomic spacing and crystallographic structure of natural and manufactured materials.

Figure 4.2b The PANanaltical XRD X'Pert PRO

Principle and working:--

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons and accelerating by applying a voltage, and these accelerated electrons incident on the target. When electrons have sufficient energy to knockout the inner shell electron, X-rays will produce. Filtering of X-rays is required to produce monochromatic X-rays needed for diffraction. Then X-rays are collimated and directed onto the sample. By rotating the sample and detector, the intensity of the reflected X-rays is recorded; when the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation [6] i.e.

$$2d\sin\theta = n\lambda$$

constructive interference occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument goniometer used to maintain the angle and to rotate the sample.

Applications

X-ray powder diffraction is most widely used:--

- To identify crystalline phases and orientation
- To determine crystal structure
- To determine lattice parameters, strain, grain size, expitaxy, phase composition, preferred orientation order disorder transformation, thermal expansion etc
- To measure thickness of thin films and multi-layers

4.2c Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) as is a microscopic technique in which a beam of electrons is transmitted through an ultra thin specimen and interacting with it. The transmission of electron beam is highly dependent on the properties of material like density, composition, etc. More no. of electrons will pass through porous material but the dense material will allow less no. of particles to pass through it. An image is produced via interaction of the electrons transmitted through the specimen. This image is magnified and focused onto an imaging device, such as a fluorescent screen. It can be detected by a sensor such as a CCD camera.

The resolving power of TEM is significantly higher than that of light microscopes, because of small de Broglie wavelength of electrons. This enables the user to examine fine detail atoms of size of few angstrom (10^{-10} m), i.e. tens of thousands times smaller than the smallest resolvable object in a light microscope. TEM have a wide-range of applications in a variety of scientific, education, research and industrial fields. TEM is used in various application in different field like in cancer research, semiconductor research, materials science, pollution and nanotechnology [7]. At smaller magnifications due to the thickness and composition of the material, the absorption of electrons in the material becomes responsible for contrast of TEM image but at higher magnifications, expert analysis of observed images is required because complex wave interactions vary the intensity of the image. Alternate modes of use allow for the TEM) to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging.

Figure 4.2c Transmission electron microscopy

As opposed to a light microscope, the wavelength of illumination that is produced by an energized beam of electrons in TEM increases greatly the resolving capabilities. The transmission electron microscope is used to characterize the microstructure of materials with very high spatial resolution. Information about the morphology, crystal structure and defects, crystal phases and composition, and magnetic microstructure can be obtained using TEM analysis. Using an electron microscope offers the advantage of increasing both the magnification of an object and the resolution over other imaging tools. The lighter areas of the image represent the places where a greater number of electrons were able to pass through the sample and the darker areas reflect the dense areas of the object. TEMs are costly, large, cumbersome instruments that require special housing and maintenance. In TEM, the information can be obtained from the real as well as from reciprocal space. They are also the most powerful microscopic tool available to-date, capable of producing high-resolution.

4.2d Energy Dispersive X-Ray Spectroscopy (EDX)

Energy Dispersive X-Ray Spectroscopy (EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. When a high energy electron beam is focused into the sample, x-rays are generated due to secondary electron transitions. These can be analyzed by the EDX technique in order to determine elements present in the sample. The EDX analyze the phases as small as 1 µm or less. All elements from atomic number 4 (Be) up to 92 (U) contained in the sample can be detected and analyzed simultaneously, but elements of low atomic number are difficult to detect by EDX.

An atom within the sample contains ground state electrons in discrete energy levels. As shown in figure1 the incident beam creates a hole by ejecting an electron from the inner shell. An electron from higher-energy shell then fills that hole as shown in figure4.2d. There is a difference in energy of the higher and the lower energy shell that may be released in the form of an X-ray. An energy-dispersive spectrometer is used to measure the number and energy of the X-rays emitted from a specimen. The elemental composition of the specimen is measured, because the energy of X-rays is characteristic of energy difference between the two shells and of the atomic structure of the elements present [8].

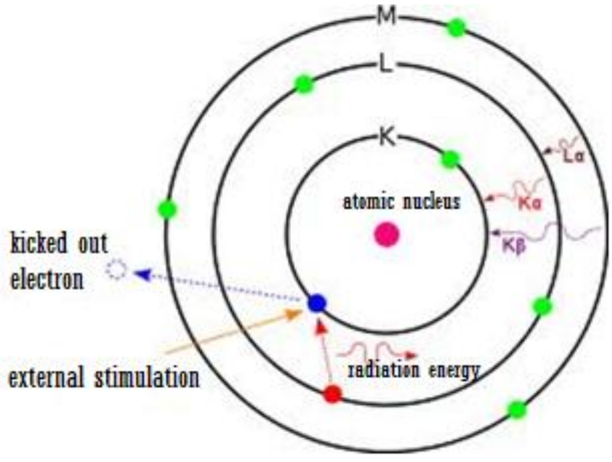

Figure 4.2d Principle of EDX

An electron beam strikes the surface of a sample. The energy of the beam is typically in the range of 10-20 KeV. Because of this X-rays emitted from the irradiated material. The energy of the X-rays emitted depends on the material under examination. The region from which X-rays are produced is 2 micron in depth that's why EDX is not a surface science technique. A 2-D image of each element in the sample can be obtained by moving the electron beam across the material.

Energy dispersive X-ray microanalysis technique has been widely used to determine the compositions of particles, contamination and thin film layers in wafer fabrication. The relative concentrations in weight, oxide, or atomic formula percentages can be obtained from the EDX spectra. Modern Detector allows for rapid analysis and concentration analysis in less than a minute. An EDX can be used in various fields like environmental testing, materials identification, home inspection metallography, etc.

4.2e Superconducting quantum interference device

A superconducting quantum interference device (SQUID) is a mechanism used to measure extremely weak signals i.e. magnetic flux. For this, SQUID uses the properties of electron-pair wave coherence and Josephson Junctions. SQUID measure a variety of physical quantities, including magnetic field, magnetic field gradient, voltage, and magnetic susceptibility because of its special flux-to-voltage characteristic. The fabrication of conventional SQUID from low-T_c metallic superconductors and the high-T_c SQUID are discussed. The low-T_c SQUID are made of niobium by sputtering and photolithography. They require a liquid Helium bath for cooling. The high-T_c SQUID may be formed by pulsed-laser deposition. The liquid nitrogen bath is used for the cooling of the high-T_c SQUID. There are two types of SQUID on the basis of a superconducting loop interrupted by either one or two Josephson junctions, the RF or DC SQUID, respectively. The major difference between RF and DC SQUID is that the DC SQUID may offer lower noise as compared to a RF SQUID. The cost of this increase in sensitivity can be the complexity of the electronics needed to operate a DC SQUID and the difficulty in fabricating two nearly identical Josephson junctions in a single device [9].

The RF SQUID System

The single junction SQUID also known as RF-SQUID the junction is shorted by superconductor path; therefore the voltage response obtain by coupling the loop to a RF bias tank circuit. Because the current is moving in two opposite directions, the electrons have the ability to perform as qubits. RF SQUID as shown in figure4.2e is coupled to the inductor of a resonant **LC** circuit, excited with a current at a resonant frequency ranging from a few tens of

MHz to several GHz. The RF voltage across the tank circuit is also periodic in the applied flux, with a period Φ_0 , enabling one to detect changes in flux of the order of 10^{-5} Φ_0.

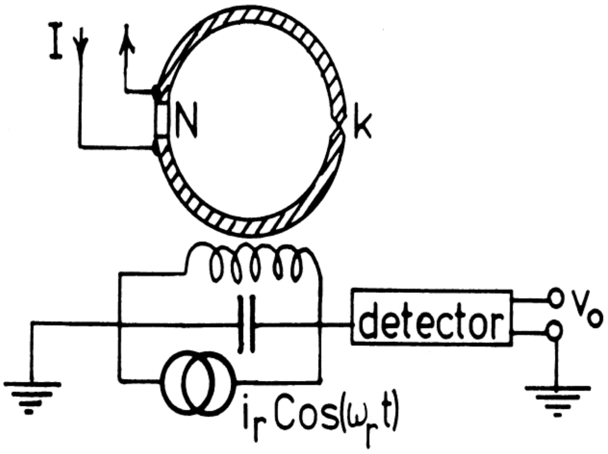

Figure 4.2e: RF SQUID system

The DC SQUID System

The double junction SQUID also known as DC-SQUID. It is based on the DC Josephson effect i.e the DC-SQUID is supplied with a constant current. Josephson junctions connected in parallel on a superconducting loop and are operated in the voltage state with a current bias. When the flux in the loop is increased, the voltage oscillates with a period Φ_0. SQUID is essentially a flux-to-voltage transducer. The change in flux typically as low as 10^{-6} Φ_0 is detected with the detection of small change in the voltage .When there is no external magnetic field, the input current I splits into the two branches equally. Because a small amount of external flux is applied to the superconducting loop, the screening currents produce the magnetic field to cancel this applied external flux. If the input current is more than I_c, then the SQUID always operates in the resistive mode

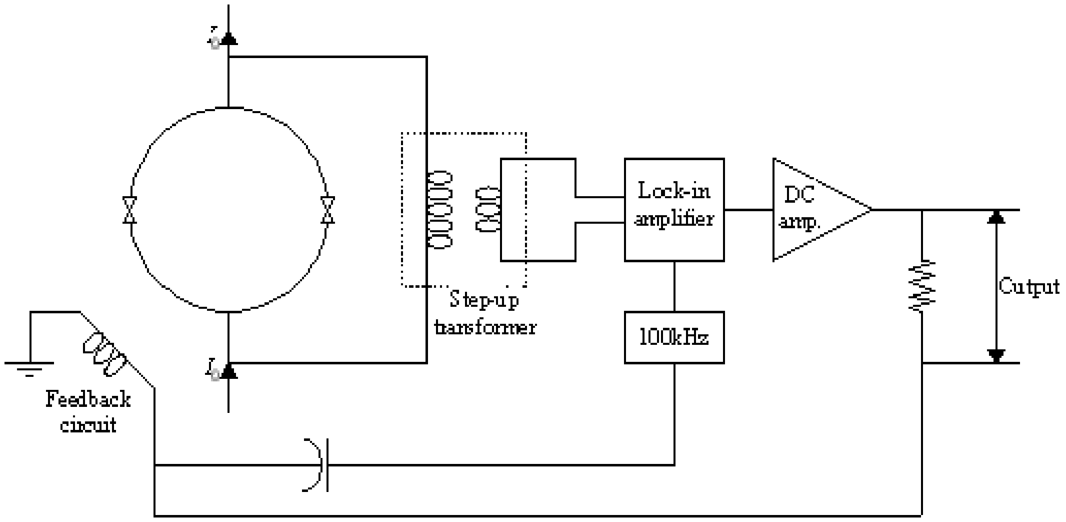

Figure 4.2e1: Schematic of a DC SQUID

Since the signal out of a SQUID is small compared with the magnitude of normal electronic signals, amplification is necessary. As shown in figure4.2e1 the lock-in amplifier is used to amplify the difference between the SQUID loop's signal and the 100 kHz signal. Fractions of a flux quantum can be measured by the feedback loop.

Applications

Systems are available for detecting magnetic signals from the heart, brain, lungs, liver stomach, eyes etc., measuring the magnetic susceptibility of materials. SQUID that is used to measure heartbeat; called a magnetocardiogram. A high-resolution image of its magnetic field structure can be obtained by scanning a SQUID probe over a sample. Oil prospecting, earthquake prediction, geothermal energy surveying, movement of the Earth's magnetic poles can be measured with the use of SQUIDs.

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Chapter 5

Results and discussion

5.1 Structural and phase analysis

The XRD pattern of pure and Co doped CdSe NPs shown in figure5.1. All the peaks are assigned to the wurtzite structure having hexagonal phase of pure and Co doped CdSe nanoparticles, (JCPDS) file no 08-0459. There is no contribution from extra phase like CoSe. The peak broadening has been observed with increase in Co concentration, which implies the incorporation of Co in the host CdSe nanoparticles. This is because of smaller ionic radii of Co^{2+} (82pm) as compare to radii of Cd^{2+} (103pm). The average crystallite size of NPs can be determined by Debye-Scherrer's formula

$$\mathbf{D = 0.94\,\lambda / \beta \cos\theta}$$

Where, D is the crystallite size, λ the wavelength of radiation used, θ the Bragg angle and β full width at half maxima.

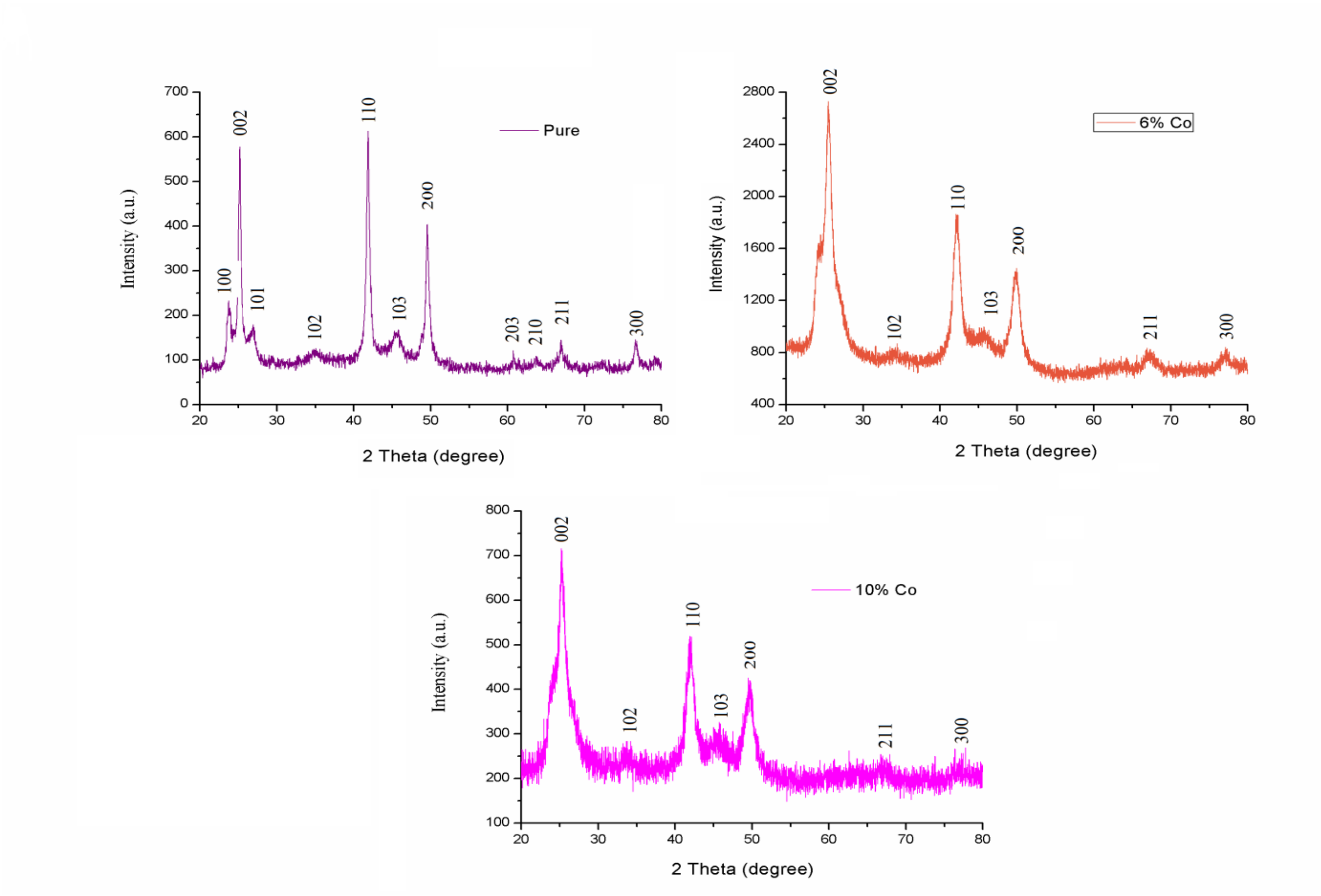

Figure5.1 The XRD pattern of pure and Co doped CdSe NPs

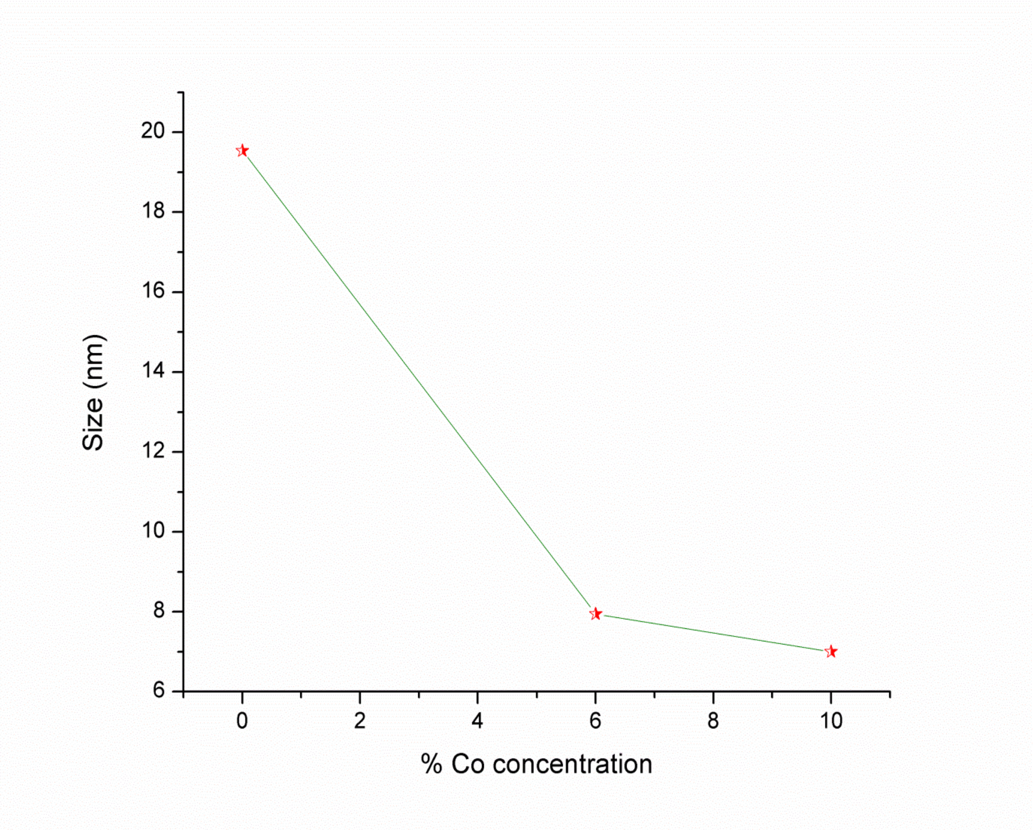

Figure5.1a The plot between % Co concentration in CdSe verses size of NPs

The variation of crystallite size with cobalt doping concentration is shown in figure5.1a. The average crystallite size comes out to be 19.5 nm, 7.9 nm, 7 nm for pure, 6%, and 10% Co doped CdSe nanoparticles. It is also clear from figure5.1a the crystallite size decreases by increasing doping concentration.

5.2 UV-Visible Spectroscopy

UV-Visible absorption spectra of pure and Co doped CdSe is shown in figure5.2. From figure it has been observed that there is a tail in the absorption spectra of pure CdSe nanoparticles which indicates the non-uniform morphology of nanoparticles [1]. However, no such tail has been observed in Co doped CdSe nanoparticles. Further, the absorption spectroscopy play an important role for the determination of band gap which can be calculated from Tauc's relation. According to the Tauc's relation, the absorption coefficient for a direct band gap material is given by [2]

$$\alpha h\nu = A\,(h\nu - E_g)^n, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (1)$$

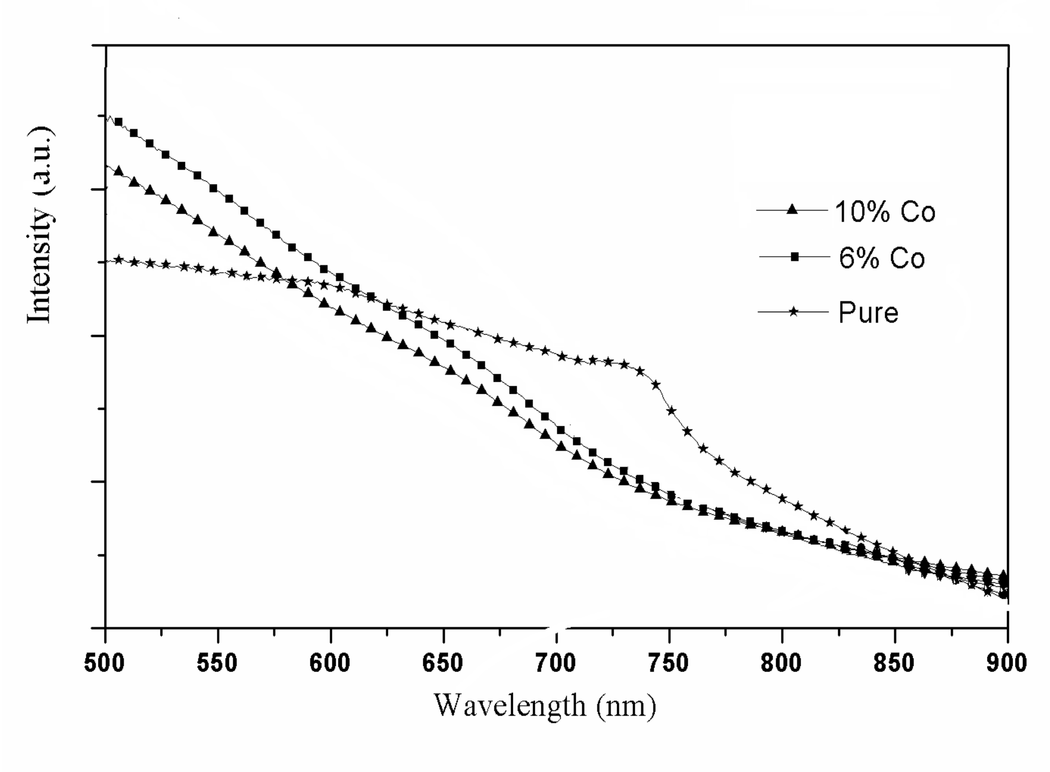

Figure5.2 UV-Visible absorption spectra of pure and Co doped CdSe nanoparticles

where Eg the energy gap, constant A, is different for different transitions, (hν) is energy of incident photon and n is a constant value, which is equal to 1 for direct band gap semiconducting materials. The figure5.1a shows the plot of $(\alpha h\nu)^2$ versus (hν). It has been

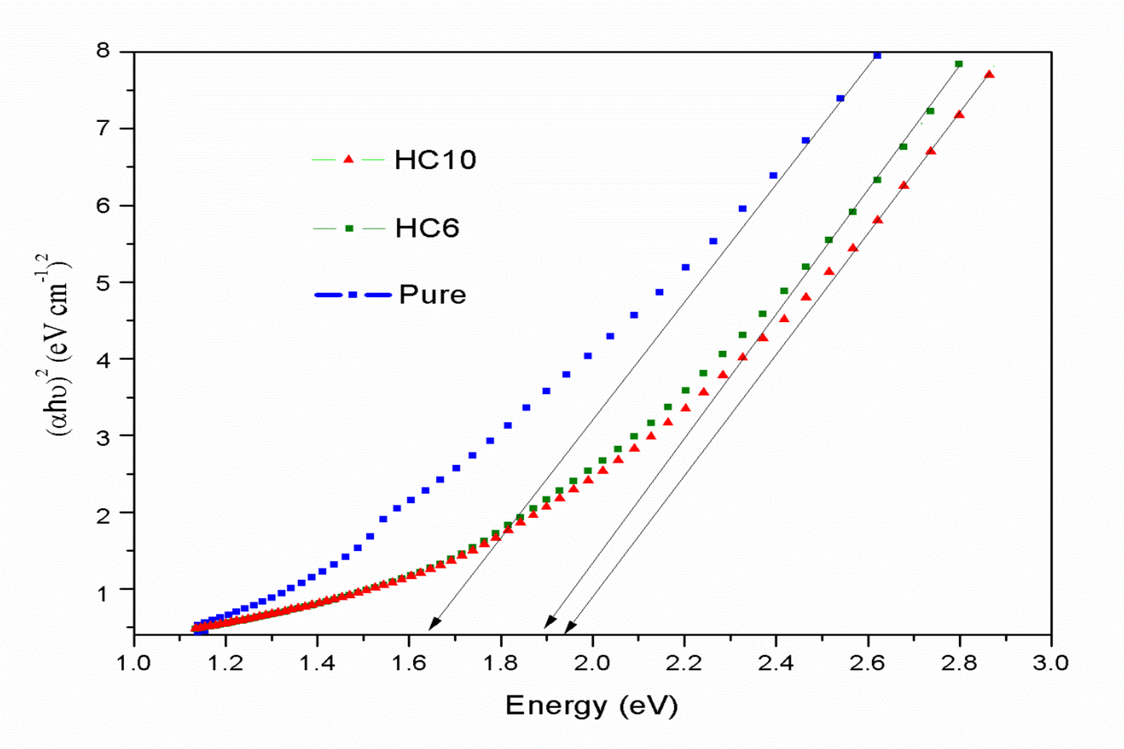

Figure 5.2a The plot between $(\alpha h\nu)^2$ and binding energy (hν)

observed from figure5.2a that the band gap values for pure, 6% and 10% Co doped CdSe nanoparticles are 1.65 eV, 1.90 eV and 1.94 eV respectively. The bulk CdSe has a band gap of 1.72 eV, pure CdSe nanoparticles are red shifted. The blue shift has been observed in the band gap with increase of Co concentration. The quantum confinement effect in nanomaterials is responsible for observed blue shift in present study.

5.3 EDX analysis

The EDX analysis of pure, 6% and 10% Co doped CdSe nanoparticles shown in figure5.3. This figure exhibits the presence of all elements in the sample i.e. cadmium(Cd), cobalt(Co), and selenium(Se) and it does not show trace of any other element. It has been observed that Cd, Se and Co are present in their stichiometric ratio. This study further shows the doping of Co in CdSe nanoparticles.

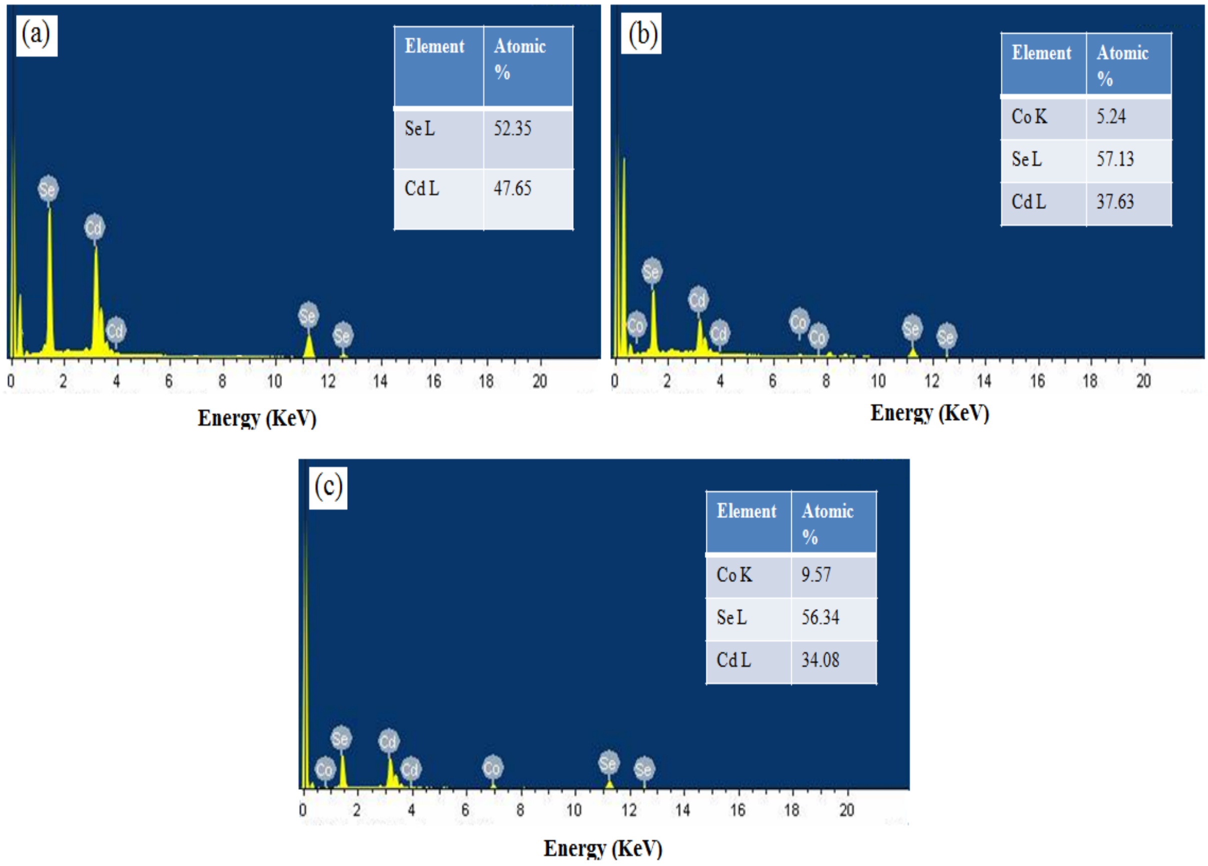

Figure 5.3 EDX of pure and Co doped CdSe nanoparticles

5.4 Morphological analysis

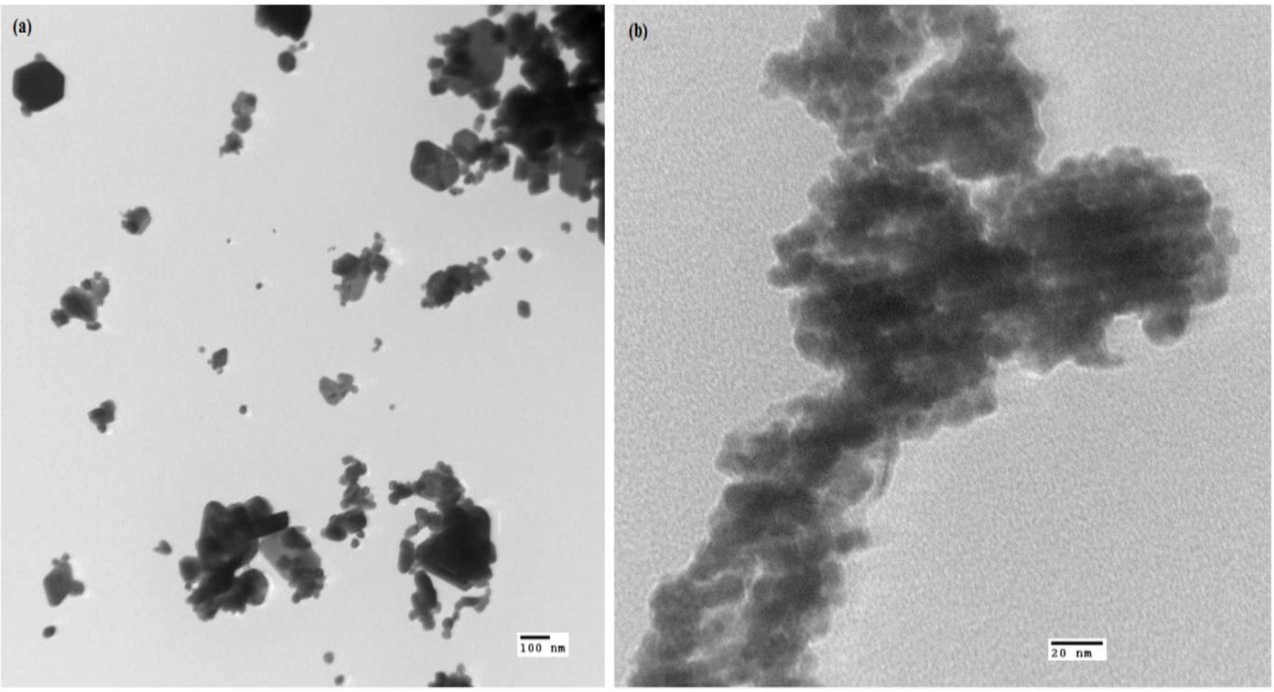

Figure5.4 TEM image of (a) pure and (b) 10% Co doped CdSe nanoparticles

The study from transmission electron microscope has been used to determine the shape and size of undoped and Co doped CdSe nanoparticles. TEM micrograph shown in figure5.4 clearly reveals the presence of non-uniform nanoparticles for pure CdSe. The Co doping in CdSe nanoparticles leads to spherical particles having very small size as compared to pure CdSe nanoparticles. The average particle size comes out to be 48nm for pure and 8nm for Co doped CdSe nanoparticles.

5.5 Magnetic study

The magnetic measurements of pure and Co doped CdSe nanoparticles shown in figure5.5 and recorded at room temperature (300K). It has been observed from M-H analysis that the pure CdSe nanoparticles show diamagnetic behavior as bulk CdSe is also a diamagnetic material but at 6% Co doping ferromagnetic behavior emerges due to long range ordering. However, at 10% Co doping leads to antiferromagnetism in CdSe nanoparticles. The Co (II) (3d7) exist in a singlet ground state having tetrahedral coordination environment in CdSe and the stronger coupling between Co d-orbitals and conduction band of the host CdSe nanoparticles lead to antiferromagntism in the host material [3].

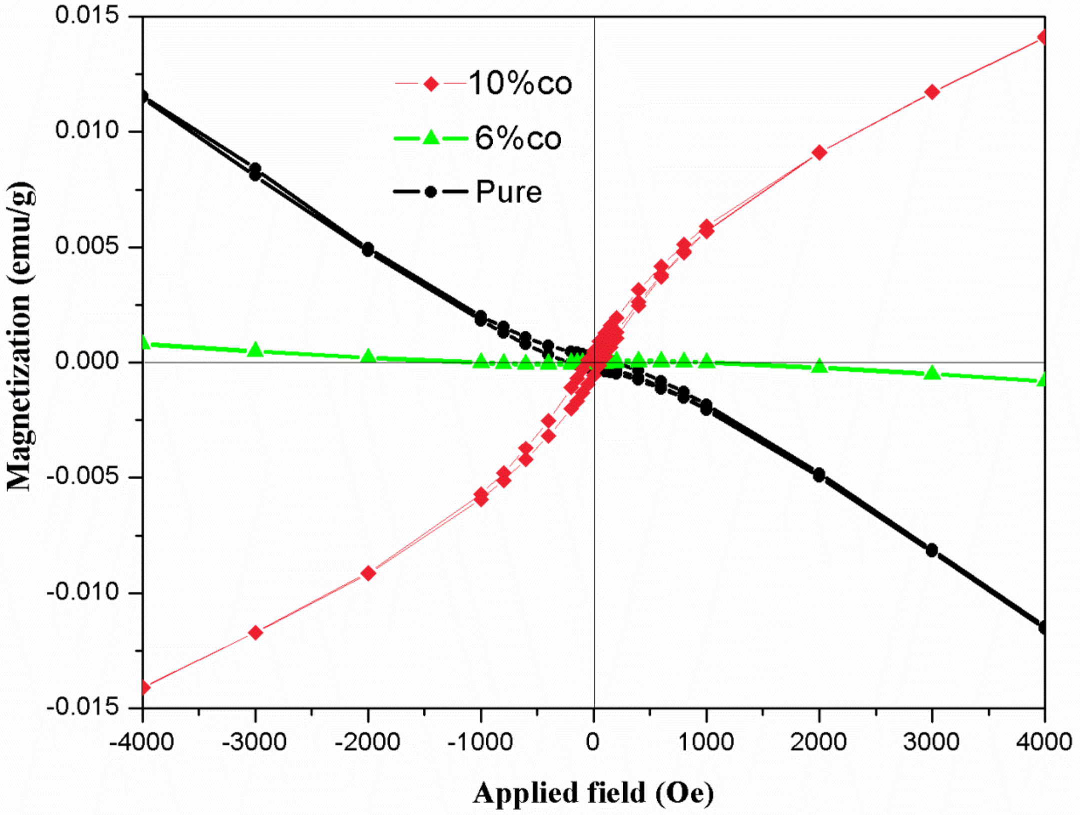

Figure 5.4 Field dependent M-H curves for pure, 6% and 10% Co doped CdSe nanoparticles.

5.6 Conclusion

In the present work, pure and Cobalt doped CdSe nanoparticles has been synthesized by solvothermal technique using SDS(sodium doceyl sulphate) as a capping agent. The effect of Co doping on structural, morphological and magnetic properties is investigated.

- All the peaks are assigned to the wurtzite structure having hexagonal phase of pure and Co doped CdSe nanoparticles, (JCPDS) file no 08-0459. The peak broadening has been observed with increase in Co concentration, which implies the incorporation of Co in the host CdSe nanoparticles. This is because of smaller ionic radii of Co^{2+} (82pm) as compare to radii of Cd^{2+} (103pm).

- The blue shift has been observed in the band gap with increase of Co concentration due to quantum confinement effect.
- EDX analysis exhibits the presence of cadmium(Cd), cobalt(Co), and selenium(Se) and it does not show trace of any other element.

- The morphological study reveals the presence of non-uniform nanoparticles for pure CdSe, but the Co doped CdSe nanoparticles leads to spherical shape of particles.

- It has been notice that the pure CdSe nanoparticles show diamagnetic behavior but due to long range ordering 6% Co doped CdSe exhibits ferromagnetic behavior. However, at 10% Co doping leads to antiferromagnetism in CdSe nanoparticles.

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