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Room-temperature ferromagnetism in CdO nanocrystalline powder co-doped with Al- and Gd: treatment in hydrogen atmosphere

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Abstract

Powders of cadmium oxide codoped with Gd and Al ions were synthesised by thermal decomposition method. The mass ratio of Al/Cd in powder form samples was maintained constant, while the mass ratio of Gd/Cd was varied systematically. The final purpose of the present study was to synthesis powders having appreciable room temperature ferromagnetic (RT-FM) properties. To achieve this task, amounts from each synthesised powder were treated in hydrogen atmosphere in order to study its effect on the physical properties, especially the magnetic properties of the samples.

The X-ray fluorescence (XRF) and X-ray diffraction (XRD) measurements confirm the purity of the as-prepared powders and the formation of a mono-phase nano-crystalline structure. Thus, the Gd and Al ions incorporated into host CdO lattice formed substitutional solid solutions (SSS). The magnetic properties of the as-prepared and hydrogenated powders were investigated as a function of % Gd doping level. It was observed that the magnetic behaviour of pure CdO transforms from diamagnetic to paramagnetic with doping by Al and Gd ions. More importantly, it was found that the treatment in hydrogen atmosphere stimulates the conversion of some CdO forming Cd metal nano-grains, resulting in transformation to ferromagnetic behaviour. For hydrogenated CdO powder doped with 3% Gd, the coercivity (H_c), remanence (M_r), and saturation magnetization (M_s) were 195.9 Oe, 0.77 memu/g, 5.1 memu/g, respectively. Therefore, it was proved, for the first time, the possibility of manufacturing CdO with stable RT-FM by doping and post treatment under hydrogen atmosphere, thus a new potential candidate to be used as a dilute magnetic semiconductor (DMS).

Dedications

بسم الله الرحمن الرحيم

To my parents, my husband and my kids.

To everyone whom I love and respect.

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Abbreviations

Vis	Visible
NIR	Near Infrared
CTO	Cadmium Tin Oxide Cd_2SnO_4
TMs	Transition Metals
DMS	Diluted Magnetic Semiconductor
RT-FM	Room Temperature Ferromagnetic
BMPs	Bond Magnetic Polarons
SSS	Substitutional solid solution (SSS)
Al^{3+}	Aluminum
Gd^{3+}	Gadolinium
SEM	Scanning electron microscope
FTIR	Fourier -transform infrared spectroscopy
E_g^{dir}	Direct energy-structural band gap
E_g^{ind}	Indirect energy-structural band gap
E_g^{opt}	Optical band gap E_g^{opt}
E_g^{FS}	Fermi level stabilization energy E_g^{MB}
E_g^{MB}	Moss-Burstein shift E_g^{MB}
Eg	Band gap
K-M	Kubelka-Munk
h ν	Photon energy

V _O	Oxygen vacancies
DM or Dia	Diamagnetic
Para	Paramagnetic
BMP	Bound magnetic polaron
EMI	Electronic medium interaction
NC	Nanocrystalline
EDXRF	Energy dispersive X-ray Fluorescence
XRD	X-ray Diffraction
DRS	Diffuse Reflectance Spectroscopy
VSM	Vibrating-Sample Magnetometer
TCOs	Transparent Conducting Oxides

CHAPTER ONE: INTRODUCTION

1.1 Introduction

1.2 Research Problem

1.3 Research Objective

1.4 Research Question

1.5 Research significance

1.6 Research setting

CHAPTER ONE: INTRODUCTION

1.1 Introduction

Transparent Conducting Oxides (TCOs) like cadmium oxides, zinc oxide, tin oxide, etc. are electrical conductive semiconductor materials with a high transmittance. They are usually prepared with thin film technologies and used in opto-electrical devices such as solar cells, displays, opto-electrical interfaces and circuitries (Aydın, El-Nasser, Yakuphanoglu, Yahia, & Aksoy, 2011; Dakhel & Hamad, 2013; Aswani et al., 2014).

Due to its high carrier mobility, high electrical conductivity and optical transmittance in the visible (Vis) and in the near infrared (NIR) regions of the spectrum, cadmium oxides (CdO), is considered as a promising metal-oxide semiconductor for manufacturing of flat-panel displays, light emitting diodes, biological labels, gas sensor and photovoltaic solar cells (Kumar et al., 2015).

Indeed, semiconductor CdO was used as a transparent conducting oxide (TCO) in 1907 by Baedeker (Barquinha et al., 2012). He has prepared films of Cd metal by evaporation in a glow discharge chamber and then oxidized it in the air atmosphere to obtain CdO, which is used to produce transparent electrode CdTe – based thin film solar cells. In the late 1970s, CdO was investigated further as a Ternary compound cadmium tin oxide Cd_2SnO_4 (CTO), which was shown to be a good TCO. Since then, the commercial values of these thin films have been recognized and the list of potential TCO materials has expanded to include Optoelectronic devices.

Pure CdO has n-type semiconducting behaviour with low resistivity (10^{-2} - $10^{-4} \Omega \text{ cm}$) due to its intrinsic structural point defects of oxygen vacancies and Cd interstitials (Bououdina & Dakhel, 2014). It was proved that the optical and conducting properties could be improved by doping of CdO with different metallic ions of ionic radii smaller than that of Cd^{2+} ions like In, Sn, Al, SC, Y, Tl, etc. Such doping compresses the host CdO lattice unit cell (Aswani et al., 2014; Aydın et al., 2011; Dakhel, 2010). Doping of CdO with Transition Metals (TMs) would transform it into Dilute Magnetic Semiconductor (DMS) by creation of Room-Temperature Ferromagnetic (RT-FM) behaviour.

The generation of ferromagnetic properties could be realised by the exchange spin-spin (**S.S**) interactions between dopant TM ions mediated with itinerant charge carriers (electrons). Another model was also proposed in which the exchange of coupling between localised dopant TM ions is realised by overlapping of Magnetic Polarons (MPs) (Dakhel, El-Hilo & Bououdina, 2014).

However, the explanation of the cause of RT-FM in DMS materials as a physical phenomenon is still challenging and needs further exploration by experimental and theoretical works, despite that there are many previous works reported in the literature with that issue. Furthermore, it is important to mention that RT-FM behaviour was also observed in undoped oxides, which were known for a long time to be dia- or para-magnetic materials, and this experimental finding is referred to as $d^0\text{FM}$. Some research findings attribute the FM to the point defects, such as oxygen vacancies (Abdel Hakeem, 2010; Aljawf, Rahman & Kumar, 2016), and even to what is called size effect (quantum effect) due to formation of nano-sized grains (particles) within the material.

It is to be mentioned here that sometimes, FM properties could appear only at very low temperatures. For example, the magnetic properties of Ni-doped CdO have been studied and established the coexistence of para and ferromagnetism at very low temperature (5 K) (Ahmad et al., 2013).

Doping of CdO with Al^{3+} ions could support the magnetic collective mutual interaction so that they are reacted as a “magnetic catalyst”. On the other hand, doping of CdO with Gd^{3+} magnetic ions could create substitution solid solution (SSS) with stable FM behaviour. These expectations will be examined experimentally in this research work.

1.2 Research Problem

Nanocrystalline CdO is one of the degenerate semiconductors with good optical transmittance and high electrical conductivity. It has a wide range of applications, especially in electronic technology and production of optoelectronic devices, including applications in solar energy systems (Aydın et al., 2011; Dakhel & Hamad, 2013). To increase the range of their applications, CdO lattice micro-structure was modified in order to create exotic properties like mechanical (hardness), magnetic...etc. It was established that hybridisation of properties could be realised and controlled through doping of CdO by ions, which have a suitable property that is needed to be appear in the host CdO. Therefore, the aim of doping of CdO with different ions is to improve their ordinary TCO functions as well as to create exotic properties that did not usually exist in the host CdO. For instance, doping of CdO with transition metal (TM) or rare-earth ions could create stable magnetic properties in order to produce (DMSs) (Sérier et al., 2012).

The present research is specified to investigate CdO powder doped with Gadolinium (Gd^{3+}) and Aluminium (Al^{3+}) ions. It becomes known that Al^{3+} ions of smaller radius (0.063 nm) than that of Cd^{2+} (0.097 nm) when doped in CdO lattice improve its electrical conduction and increase its optical band gap (Wongcharoen, Gaewdang, & Wongcharoen, 2012; Kumaravel, Menaka, Snega, Ramamurthi, & Jeganathan, 2010). Furthermore, it is known that Gd^{3+} ions as rare-earth ions could also be used as dopant in order to improve the CdO electrical conduction parameters (Pan, Li, & Lian, 2013) and to introduce magnetic properties by creating diluted magnetic semiconductors (DMS) (Bououdina & Dakhel, 2014). Thus, one can expect that doping CdO nano-powder with both Al and Gd ions can create useful optical, electrical and magnetic properties.

However, the present study focuses on the structural, optical and magnetic properties of Al- and Gd- co-doped CdO powder samples with fixed Al content and different content of Gd dopant. Also, we investigate the effect of annealing in hydrogen atmosphere (hydrogenation) on the structural, optical, and magnetic properties of the host CdO powder.

1.3 Research Objectives

The main objectives of this thesis are as follows:

- Creation of room-temperature ferromagnetic properties in cadmium oxide (CdO) nanocrystalline powder by means of doping with Aluminium (Al) and Gadolinium (Gd) ions.
- Study the structural, optical and magnetic properties of Al-Gd Co-doped CdO Nano powder.
- Study the effect of annealing in hydrogen atmosphere on the properties of Al-Gd co-doping CdO nano-powder.

1.4 Research Questions

- What are the properties of pure cadmium oxide nano-crystalline powder?
- What is the influence of doping with Aluminum and Gadolinium ions on the physical properties of CdO nano-powder?
- Is it possible to create room temperature ferromagnetic properties in CdO nano-crystalline powder?
- What is the effect of hydrogenation on the Al-Gd co-doping CdO nano-powder?

1.5 Research Significance

Doping of CdO with magnetic ions, such as Al^{3+} and Gd^{3+} , in order to combine some stable magnetic properties together with its normal optoelectronic properties, which could produce different novel applications.

The main purpose of this research is to investigate the possibility of using CdO co-doped with Al and Gd ions in order to produce room-temperature ferromagnetic (FM) properties of strength that depends on Gd doping level. The results may highlight the usage of CdO as a DMS and provide more clear understanding of the RT-FM phenomenon in DMS-like oxides. On the way of understanding the DMS-like phenomenon, the effect of hydrogenation on the magnetic properties of RT-FM could also be investigated in order to provide an opportunity to conduct a new kind of physical research.

1.6 Research Setting

The subject of the present study investigates the effect of doping with Al and Gd ions on the structural, optical and magnetic properties of CdO nano-powder. The study constrains by many factors like missing some tools such as scanning electronic microscope (SEM).

CHAPTER TWO: Background Theory and Literature Review

2.1 Cadmium oxides and Related Compound and Literature Review: General Properties

2.1.1 CdO Structure

2.1.2 CdO Optical Properties

2.1.3 Doping of CdO NC

2.1.4 Room-Temperature FM in CdO NC

2.1.5 Hydrogen treatment in doped CdO NC

2.2 Synthesis Methods for Metal Oxide Nanoparticles

2.2.1 Thermal Decomposition

2.1 Cadmium oxides and Related Compounds

Literature Review: General properties

Cadmium Oxide (CdO) is the first discovered transparent conducting oxide semiconductors. Its excellent optical and electronic properties have made it one of promising materials for flat panel displays, photodiode, phototransistor, photovoltaic cells, transparent electrodes, IR detector and antireflection coat (Chandiramouli & Jeyaprakash, 2013; Dakhel, El-Hilo & Bououdina, 2014; Kumar, Ojha, & Walkenfort, 2016; Kumar, Layek, Yashpal, & Ojha, 2015).

In this chapter, we will introduce the physical properties of pure CdO nano-crystalline (NC) powder, the effect of dopant magnetic ions and its application.

2.1.1 CdO Structure

Cadmium oxide (CdO) is a degenerate n-type semiconductor. It is predominantly ionic bonded. However, it usually exists with non-stoichiometric composition (Chandiramouli & Jeyaprakash, 2013). CdO has the rock-salt crystal structure (FCC) in which each Cd or O ion is surrounded by 6 neighbours with octahedral cation interstitials and O ion anion vacancies, resulting in free electron concentration of 10^{19} - 10^{21} cm⁻³. CdO has cubic structure of Fm-3m space group as shown in Fig 2.1. The Shannon ionic radius of Cd²⁺ is 0.095 nm for coordination number CN=6. The lattice parameter (a) is 0.4695 nm (Dakhel & Hamad, 2013; Dakhel et al. (2014)).

CdO crystal color can be varied from brown to orange –yellow depending on the cadmium ion concentration. The color also varies with respect to the particle size. (Chandiramouli & Jeyaprakash, 2013).

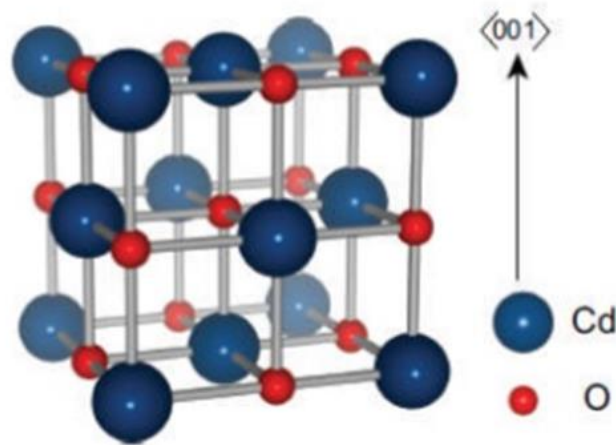


Fig 2.1: CdO-Crystalline Structure.

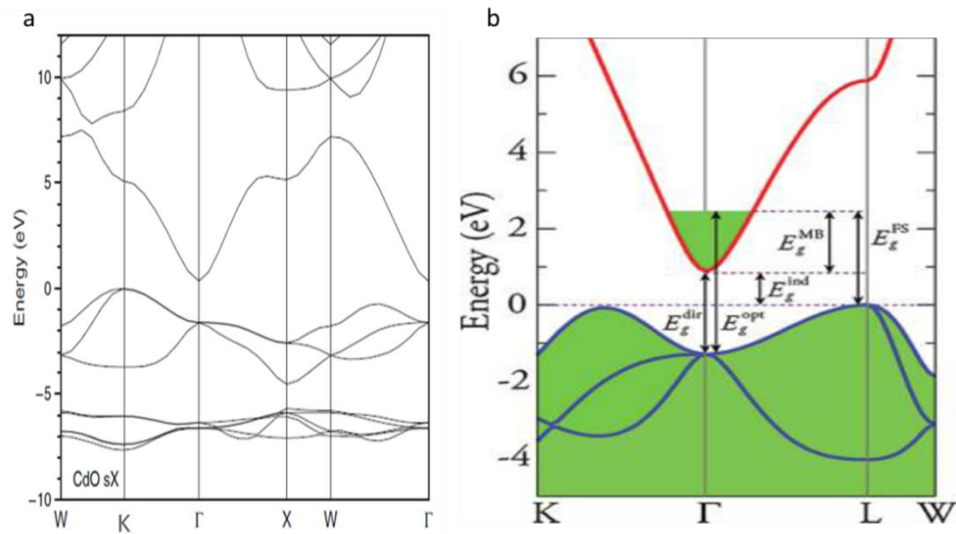


Figure 2.2: a. Band structure of CdO using the screened exchange method, b. Illustrative image of CdO structure.

Figure 2.2 shows the CdO electronic band structure as calculated by the screened exchange method. It gives a reasonable band gap compared

to experiment. Also, it shows the direct energy-structural band gap (E_g^{dir}), the indirect energy-structural band gap (E_g^{ind}), the optical band gap (E_g^{opt}), Fermi level stabilization energy (E_g^{FS}) and the Moss Burstein shift (E_g^{MB}). The shaded areas indicate occupation by electrons. The valence band maximum is set to 0 eV. In CdO band structure the indirect band gap due to pd-repulsion except at Gamma point Γ , where it is due to octahedral symmetry. It shows the minimum gap at 0.8 eV (Dakhel, 2009). The conduction band minimum is at Γ , free-electron-like, and is formed from Cd s states. Cadmium oxide shows a narrow direct band gap E_g^{dir} of ~ 2.3 eV, which makes it to be photoactive (Kumar et al. 2016; Sivakumar et al. 2015).

However, the valence band maximum is not at Γ , it is at the L point and along Γ W. This leads to a calculated minimum indirect gap of 0.6 eV and a minimum direct gap of 2.1 eV, compared to experimental values of 0.8 and 2.3 eV, respectively (Ginley, 2010).

The CdO with donor some electrons would be at the lower energy of the conduction band. This causes increase in the optical band gap, which is called Moss-Burstein shift, and varies inversely with the effective mass (Chandiramouli & Jeyaprakash, 2013).

2.1.2 CdO Optical Properties

Wide band gap of CdO (2.3eV) can lead to new applications in optoelectronic, electronic and photo catalytic devices.

It was established that the band gap (E_g) can be measured from the diffuse reflectance spectra (DRS) of CdO power samples (Aydin et al., 2011). To calculate the accurate values of the band gap of pure and doped

CdO NC, the reflectance value should be converted to absorbance by applying the Kubelka-Munk (K-M) function given by Eq (2.1) (Jentoft F. G. 2004). The K-M function, which is generally used to analyze the diffuse reflectance spectra obtained from powder samples, is written as:

$$\frac{K}{S} = \frac{(1-R_{\infty})^2}{2R_{\infty}} = F(R_{\infty}) \quad (2.1)$$

where, $R_{\infty} = R_{\text{sample}}/R_{\text{standard}}$ means the spectral diffuse reflectance of thick sample (R_{sample}) as measured relative to the standard reflectance (R_{standard}). S is the scattering coefficient, K is the so-called K-M absorbance, which is related to the absorption coefficient α by $K=2\alpha$, and $F(R_{\infty})$ is the K-M absorption function. By considering S as a constant with respect to the wavelength, therefore $F(R_{\infty}) \sim \alpha$.

Furthermore, the K-M absorbance spectra can be used to estimate the values of the optical bandgap E_g through Tauc plot technique, i. e. by using:

$$(F \cdot hv)^{2/n} = A (hv - E_g) \quad (2.3)$$

where h is Plank's constant, v is the frequency of the incident photon, A is the constant of the sample, E_g is the optical band gap of the sample, and the exponent n is equal to 1 for direct permissible transitions and 4 for indirect permissible transitions. According to the Tauc technique, the straight line portion of the plot between $(\alpha hv)^2$ vs. hv (phonon energy) is extrapolated to line, $(\alpha hv)^2 = 0$ in order to obtain the value of E_g . For example, fig. 2.3 shows the plot of $(\alpha hv)^2$ vs. hv (photon energy) for CdO:Al films as a function of doping level. The optical band gap is determined by the extrapolation method.

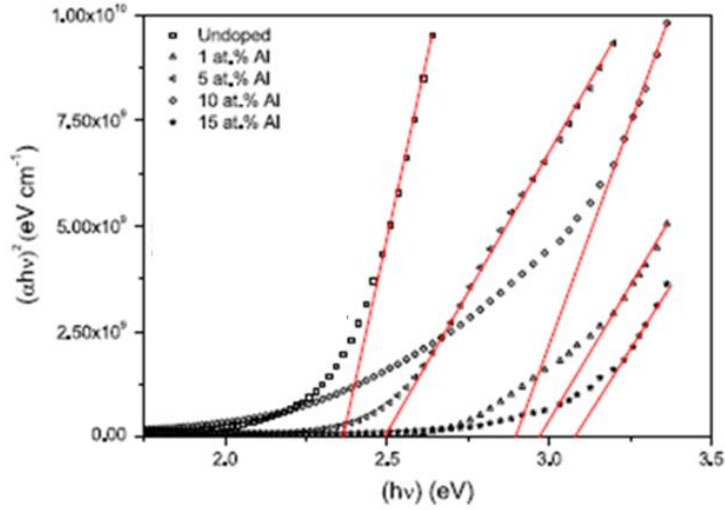


Fig 2.3: the plot of $(\alpha h\nu)^2$ vs. $h\nu$ (photon energy) for CdO: Al films prepared with Al content of 0, 1, 10 and 15 at% (Ziabari, 2014).

2.1.3 Doping of CdO crystal

Incorporation of ionic dopants in lattice of transparent conducting oxides (TCO) like CdO is aimed to vary its physical properties or introducing some exotic properties in order to bring out more novel applications and technologies. Therefore, researchers have been going on to examine how to incorporate some dopant ions that can influence the internal structure including crystallite sizes that strongly affect the physical properties of those materials (Ogale, Venkatean and Blamire, 2013). It was established that certain impurities could strongly modify the electronic and optical properties of host TCOs like CdO. Furthermore, they can create in CdO exotic properties of magnetic or mechanical origin that would extend its applications.

It was understandable that doping of CdO can simply manage the natural intrinsic structural defects, such as oxygen vacancies (V_O) and Cd

ions interstitials. These structural defects can control and might enhance the electrical conduction among other physical properties like carrier concentration and their mobility (Barquinha et al.).

There are many reports in literature, which indicate enhancement of electrical conduction parameters and optical transparency of CdO under doping with metallic ions like (In, Sn, Al, Ti, Fe, Cu, Bi, Ge, Mn, Cr), none metallic ions (F, B, Te, Si), and rare earth ions (Ce, Sm, Eu, Gd, Dy). (Aydın et al.,2011;Benhaliliba et al.,2012; Barnes et al.,2001; Dagdele et al.,2012;Dagdelen, F., Serbetci, Z., Gupta, R., &Yakuphanoglu, F.(2012); Dakhel, 2009a, 2009b, 2009c, 2010a, 2010b, 2011a, 2011b, 2014; Dakhel & Hamad, 2013; Kumar, Layek, Yashpal, & Ojha, 2015; Gupta, Ghosh, Patel, Mishra, & Kahol, 2008; Manjula, Pugalenth, Nagarethinam, Usharani, & Balu, 2015; Wongcharoen, Gaewdang, & Wongcharoen, 2012; Zhao, Morel, & Ferekides, 2002; Zheng, Lian, Zhao, & Jiang, 2011).

In the present work, Al^{3+} and Gd^{3+} dopant ions were taken into consideration to be efficient dopants for CdO, as Al^{3+} has smaller ionic radius while Gd^{3+} has almost same size that of Cd^{2+} ions (the ionic radii of Cd^{2+} and Al^{3+} and Gd^{3+} are 0.095 nm, 0.068 nm and 0.094 nm, respectively (Shannon, 1976).

It was expected that Al^{3+} ions dopants could improve the electronic conductivity, carrier concentration and mobility (Wongcharoen, et al, 2012; Kumaravel et al, 2010). Thus, it could support the magnetic collective mutual interaction and reacted as a “magnetic catalyst”. On the other hand, doping of CdO with Gd^{3+} magnetic ions could create substitutional solid solution (SSS) with RT-FM behavior (Bououdina & Dakhel, 2014).

2.1.4 Room-Temperature FM in CdO

It was established for a long time that pure, un-doped CdO has diamagnetic (DM) properties at room temperature (Chandiramouli and Jeyaprkash, 2013).

Recently, Bououdina (2014) and Dakhel (2013) observed very weak RT-FM with undoped CdO nanoparticles synthesized by thermal decomposition method. Such experimental finding was referred to as d^0 FM phenomenon, i.e. zero-doping FM. It was explained as originated from oxygen and cadmium vacancies. Moreover, some other researchers have also attributed the d^0 FM observation to point defects, such as oxygen vacancies (Abdel Hakeem, 2010), and even to what so called size effect (quantum effect) due to the formation of nano-sized grains (particles) within the material and grain boundary area (Bououdina, Song, Azzaza, 2016). Furthermore, it was observed that with codoping CdO NC powder by Gd and Cu ions, the host CdO obtained PM properties where the susceptibility (χ_p) increases with Gd doping level (Bououdina et al, 2014). However, when the Gd doping level reached 3.1%, a FM component appeared overlapped with PM. It is impressive to mention here that Gd-doped ZnO powder show RT-FM properties at level 3.5% Gd (Dakhel and El-Hilo, 2010). Other studies established formation of Super-paramagnetic behavior by annealing of Gd (0.08 at%)-doped ZnO sample at 300°C (Roqan, Aravindh & Venkatesh, 2017). Moreover, Mn-doped CdO showed only PM properties even at 5K (Ahmad et al., 2013), Cu-and Fe-codoped CdO showed PM overlapped with small FM behavior (Dakhel, El-Hilo Bououdina, 2014).

In the present work, CdO crystal is considered as a medium for doping of Gd ions, which act as magnetic sources in order to create stable dilute magnetic semiconductor (DMS) according to the sketch in figure 2.4. Theoretical models of magnetism in DMSs have suggested that the generated FM properties could be realized through the spin-spin ($\mathbf{S.S}$) Heisenberg exchange interactions between dopant TM ions mediated by itinerant charge carriers (electrons). This is called carrier-induced FM model, see sketched in figure 2.5. Another model called the Bound Magnetic Polaron (BMP) model was proposed, in which the spin-spin Heisenberg interactions necessary to produce the FM properties would be generated by super-exchange interaction via oxygen vacancies (V_o) that captured polarons (electrons), as sketched in figure 2.6. The induction of structural V_o can manage the electronic medium for interaction (EMI) of the doped crystal (Kaminski, A. and Das Sarama, 2002).

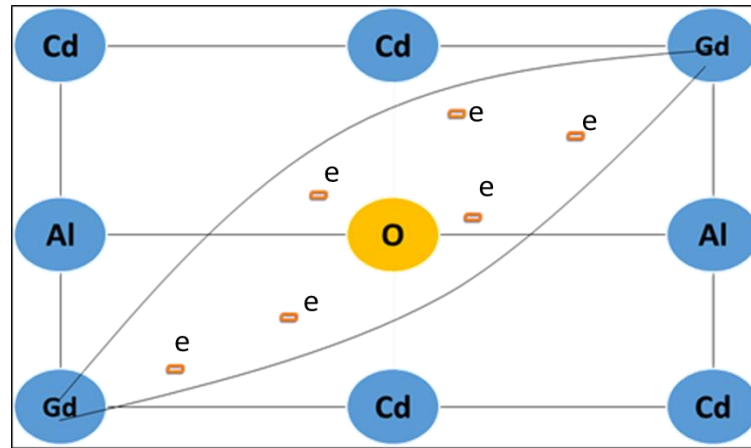


Figure 2.4: Gd ions in CdO crystal which act as magnetic sources in order to create stable dilute magnetic semiconductor (DMS).

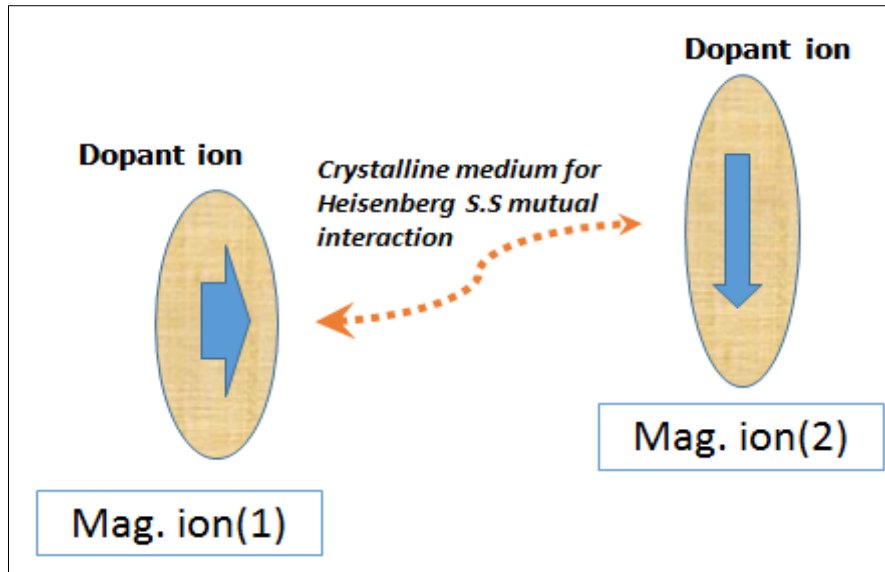


Figure 2.5: Carrier-induced FM model

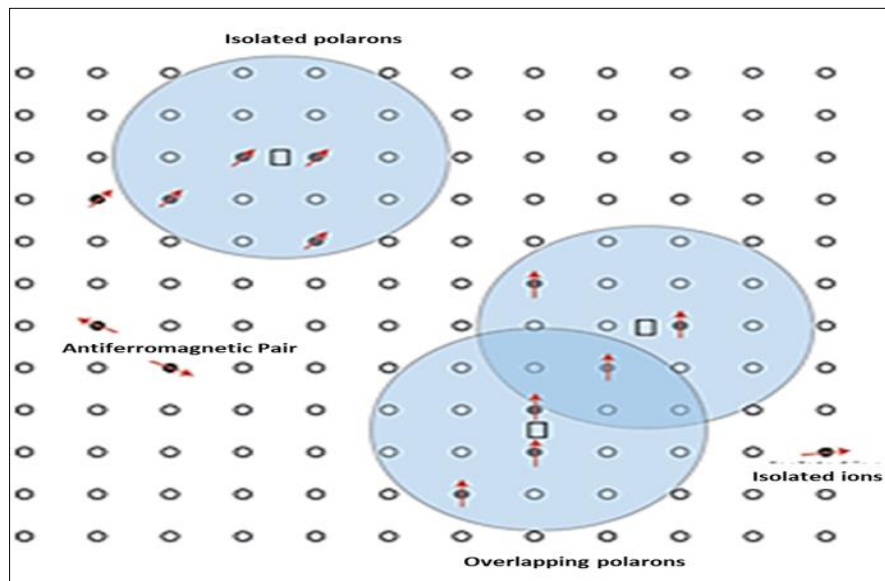


Figure.2.6: Bound Magnetic Polaron (BMP) theory

Finally, it is to mention here that FM properties sometimes could appear only at low temperatures. For example, the magnetic properties of Ni-doped CdO were studied, where it was found the coexistence of Para

and ferromagnetism at a very low temperature (5 K) (Ahmad, Khatoon, Coolahan & Lofland, 2013).

2.1.5 Hydrogen treatment of un-doped and doped CdO NC

The hydrogenation of CdO crystals means annealing of the sample in hydrogen atmosphere under certain conditions (temperature and duration).

One of the possible methods to develop the EMI in the host crystals is to induce structural O-vacancies (V_o), through which super exchange interactions can occur. Those V_o can be created by annealing the sample in hydrogen atmosphere under certain conditions. This is necessary to catalyze the interaction with structural oxygen. The dissociation of molecular hydrogen into hydrogen atoms could happen when TM ions are used as dopants playing a catalytic role (Pozzo and Alfe, 2009), and this is fundamental for S.S exchange interaction (Dakhel and Al-Najar, 2017). Moreover, the hydrogenation process physically affects the samples by eliminating native structural defects such as dangling ions/atoms/bonds and dislocations (Dakhel, 2016), which improve the EMI medium to carry the long range **S.S** interactions, necessary to create FM interactions.

According to previous experiments on annealing of CdO in H_2 atmosphere, Dakhel (2008) reported that the hydrogenation could compress the CdO unit cell and widen the band gap. Moreover, the hydrogenation has a great effect on the electrical properties by increasing the conductivity, mobility and effective concentration of carriers. The greatest enhancement in electrical parameters was found to occur with hydrogenation at 300°C for almost 30 min (Dakhel, 2008, 2011; Dakhel and Hamad, 2013). Bououdina et al (2014) have synthesized CdO

codoped with Cu and Gd powders by thermal co-decomposition and post-annealed in hydrogen atmosphere. The host CdO powder gained PM properties that increased with increasing the content of Gd ions and that the hydrogenation could create RT-FM properties especially with 3.1% Gd doping level, where the coercivity (H_c), remanence (M_r) and saturation magnetization (M_s) were 283.2 Oe, 2.04 memu/g and 6.67 memu/g, respectively. Moreover, it was observed that the hydrogenation of CdO samples at 350°C for 20 min induced a reduction of CdO forming pure metallic Cd nanoparticles. Then, the resulted FM behavior was created with strength that increased with doping level by Cu and Fe ions (Dakhel et al, 2014), Co and In ions (Dakhel and Al-naser ,2016), or Tb ions (Dakhel,2016) .

The paramagnetic (PM) susceptibility of a sample could be calculated by applying PM Curie equation (Smallman & Bishop, 1999) for volume susceptibility (χ_v) in cgs units.

$$\chi_v = N\mu^2/3k_B T \quad (2.4)$$

where N is the number of dopant ions per unit volume, μ is the effective magnetic moment of the ion, k_B is the Boltzmann constant and T is the working temperature.

The saturation magnetization (M_s) of a sample could be calculated by using the following equation (Smallman & Bishop, 1999):

$$M_s = N\mu \quad (2.5)$$

Where μ is the effective magnetic moment per ion, and N is the concentration of dopant magnetic ions.

2.2 Synthesis Methods for CdO NCs:

It was stated that the physical and chemical properties of any CdO substance are related to its particles size and shape, which are dependent

on the preparation methods and artificial conditions (Yufanyi et al., 2014). Various artificial methods have been used to synthesize CdO nanoparticles in order to obtain specific properties, some of which include chemical vapor deposition (Zhao et al., 2002), hydrothermal technique (Askarinejad and Morsali, 2009), Sol gel method (Aydin et al., 2011) solvo-thermal process (Kaviyarasu et al., 2014; Dakhel et al., 2017), thermal evaporation (Wongcharoen et al., 2012), pulse laser deposition (Zheng et al., 2011) co-precipitation (Dakhel et al., 2010), mechanochemical process (Tadjarodi and Imani, 2011), and micro-emulsion (Dong and Zhu, 2003). Some researchers have tried to modify several techniques for the preparation of CdO thin films with the aim to improve chemical and physical properties of this material which include thermal decomposition (Yufanyi et al., 2014) and MOCVD (metal-organic chemical vapour deposition) (Gulino et al., 2010), radio-frequency sputtering (Ueda et al., 1998).

2.2.1 Thermal Decomposition

The simplicity of using thermal decomposition method of synthesis of CdO NCs suggests that it can be applied on industrial scales as cheap and convenient way. Thermal decomposition involves decomposition of some precursor dissolved at high boiling point.

CHAPTER THREE: METHODOLOGY

3.1 Materials and Equipment

3.2 Synthesis of Gd/Al doped CdO nano-powders using Thermal de-composition (TDC) Method

3.2.1 Preparation of Gd/Al doped CdO nano-powders

3.2.2 Gd/Al doped CdO nano-powders annealing under hydrogen atmosphere

3.3 Energy dispersive X-ray Fluorescence (ED-XRF)

3.4 X-ray Diffraction (XRD)

3.5 Diffuse Reflectance Spectroscopy (DRS)

3.6 Vibrating-Sample Magnetometer (VSM)

This chapter presents the method used to synthesize pure and doped CdO samples. Three Gd- and Al- codoped CdO nano-powder samples of different amounts of Gd^{3+} dopants ions were synthesised in the present work and identified by their relative contents of CdO, Al and Gd. Table 3.1 presents the list of all precursor materials used to synthesis the present-work samples of different amounts of Gd/Cd mass ratio and fixed Al/Cd mass ratio. These samples were characterised by X-ray fluorescence (XRF), X-ray diffraction (XRD), UV-VIS spectrophotometer, and Vibrating sample magnetometer methods.

3.1 Materials and Equipment

The research is based on the following; three different synthesized samples of CdO nano-powder co-doped with Gd and Al using thermal decomposition method.

The starting material complexes are:

1. Cadmium acetate dihydrate $Cd(CH_3COO)_2 \cdot 2H_2O$
2. Gadolinium acetate $Gd(C_2H_3O_2)_3$
3. Aluminum nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$.

Table 3.1 below shows the used masses of the three samples;

CdO:Al:Gd (1.5%), CdO:Al:Gd (3%) and CdO:Al:Gd (6%). The Al content in each sample was fixed constant while the gadolinium was systematically controlled.

Table 3.1: The material used to obtain Sample CdO nano-powder sample doped with Gd and Al ions.

N o.	Sample's Name	Mass of Cd acetate dihydrate (grams)	Mass of Al nitrate nonahydrate (grams)	Mass of Gd acetate (grams)	Al/Cd mass ratio (%)	Gd/Cd mass ratio (%)	Gd/Cd molar ratio (%)
1	CdO:Al:Gd 1.5%	1.5	0.0323	0.034	0.5	1.5	1.06
2	CdO:Al:Gd 3%	1.5	0.035	0.064	0.5	3	2.13
3	CdO:Al:Gd 6%	1.5	0.0323	0.1274	0.5	6	4.26

From Table 3.1 it is observed that Al/Cd mass ratio in each sample remained constant (0.5 wt %) while the Gd/Cd mass ratio systematically varied as 1.5%, 3% and 6%.

Table 3.2 shows the materials used to prepare CdO nano-powder doped with Al and Gd ions.

Table 3.2: List of Materials used while the samples being prepared

Materials	Description	Characterization
Methanol	Transparent liquid	CH ₃ OH Purity%:99%
Gadolinium(III) acetylacetonate hydrate	White powder	Formula: Gd(C ₅ H ₇ O ₂) ₃ .xH ₂ O
cadmium acetate dihydrate	Brown powder	Formula: Cd(CH ₃ COO) ₂ · 2H ₂ O
Aluminum Nitrate nonahydrate,	White powder	Formula: Al(NO ₃) ₃ ·9H ₂ O
ceramic crucible	Porcelain	-
Hotplate stirrers	Plate coated glass ceramic with temperature control	Power magnet and motor give stirring speed upto1500rpm
Stirring bars	Encased in PTFE	Magnetic
Analytical balance	Capacity 110g	Readability 0.0001g
Muffle Furnace	Digital Controller & Venting Port	Temperature 1200°C- Maximum under an

		hour
quartz flask	glass	-
Hydrogen gas cylinder	Compressed gas	H ₂ gas
Manual hydraulic press	Steel	Pressure force 750Mpa

3.2 Synthesis of Gd/Al-codoped CdO nano-powders using Thermal de-composition (TDC) Method

3.2.1 Preparation of Gd/Al doped CdO nano-powders

The procedure was done as follow; First, a mixture of controlled amounts of the above complexes, shown in Table 3.1, were totally dissolved, in a small amount of methanol, in a ceramic crucible by using continuous magnetic stirring at room temperature as shown in Figure 3.1a.



a



b

Figure 3.1: **a** The dissolved mixture in methanol by using continuous magnetic stirring heater. **b** The gel that was obtained.

The stirring procedure continued for ~ 1 hour, and then the temperature was increased slowly to $\sim 90^{\circ}\text{C}$ until a gel was formed as shown in Figure 3.1b. Then, the obtained gel in open ceramic crucible was flash sintered in a furnace at 600°C for 1 hour, and cooled naturally with the furnace to the room temperature, as shown in Figure 3.2. The sintering led to the total dissolving and crystallization of the gel formation the desired solid solutions (SSs). Finally, the resulted powders were grounded and pelletized using 750 Mpa as shown in Figure 3.3.



Figure 3.2: The gel was flash sintered in a furnace at 600°C for 1 hour.



Figure 3.3: The resulting powders were pelletized using Manual hydraulic press.

3.2.2 Hydrogenation of Gd/Al codoped CdO nano-powders

For hydrogenation, part from each as-prepared powder sample was annealed in closed hydrogen atmosphere under two conditions; the first hydrogenation (H) was carried out at 300°C for 30 minutes and the second hydrogenation (HH) was carried out at 350°C for 30 minutes.

The procedure of annealing of the powder was conducted as follows; A small amount of fine powder was put in aluminum foil and inserted in a quartz flask. The flask was then fully filled with pure hydrogen gas. The flask should be closed tightly with extra clip to prevent hydrogen gas from leaking out during heating, as shown in Figure3.4.

The powder in closed flask was annealed in the furnace at 300°C for 30 minutes. After that, the powder (H) was cooled and pelletized by 750 Mpa using manual hydraulic press shown in Figure 3.3, for characterisation. Then, the same samples were re-annealed in hydrogen gas for the second time (HH) at 350°C for 30 minutes.

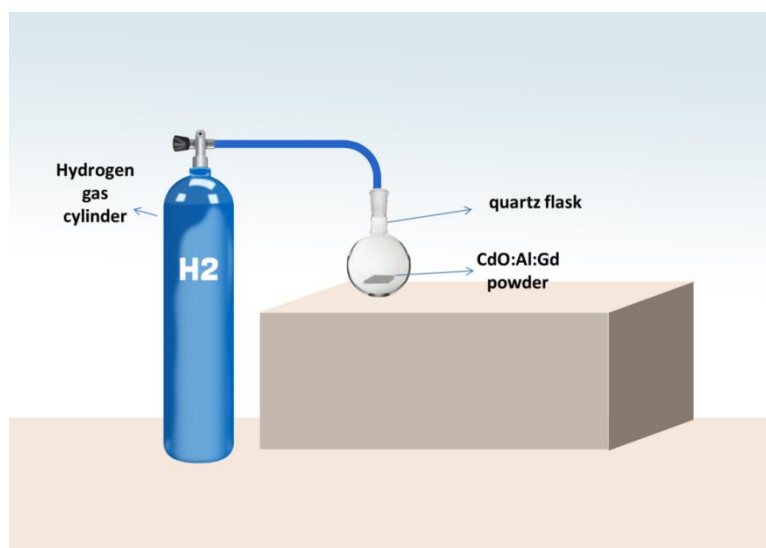


Figure3.4: amount of as-prepared powder inserted in the quartz flask and filled with pure hydrogen gas.

Table 3.4 presents all as-synthesized powders of Al/Gd co-doped CdO NCs with their preparation condition. Notice that the samples hydrogenated at 300 °C /30min were indicated by letter H and by HH to the samples that hydrogenated twice.

Table 3.4: Preparation conditions for each sample investigated in the present study.

Sample	Description of preparation conditions
CdO:Al:Gd 1.5%	1.5% Gd and 0.5%Al Co-doped CdO nanopowders (CdO:Al:Gd 1.5%) synthesized in air at 600 °C/1h
CdO:Al:Gd 1.5%H	Hydrogenated CdO:Al:Gd 1.5% powder at 300 °C for 30 minutes
CdO:Al:Gd 1.5%HH	CdO:Al:Gd 1.5% powder hydrogenated at 300 °C for 30 minutes, followed by re-hydrogenation at 350 °C for 30 minutes
CdO:Al:Gd 3%	3% Gd and 0.5%Al co-doped CdO nano-powders (CdO:Al:Gd 3%) synthesized in air at 600 °C/1h
CdO:Al:Gd 3%H	Hydrogenated CdO:Al:Gd 3% powder at 300 °C for 30 minutes
CdO:Al:Gd 3%HH	CdO:Al:Gd 3% powder hydrogenated at 300 °C for 30 minutes, followed by re-hydrogenation at 350 °C for 30 minutes

CdO:Al:Gd 6%	6% Gd and 0.5%Al co-doped CdO nano-powders (CdO:Al:Gd 6%) synthesized in air at 600 °C/1h
CdO:Al:Gd 6%H	Hydrogenated CdO:Al:Gd 6% powder at 300°C for 30 minutes
CdO:Al:Gd 6%HH	CdO:Al:Gd 6% powder hydrogenated at 300°C for 30 minutes, followed by re-hydrogenation at 350°C for 30 minutes

3.3 Energy dispersive X-ray Fluorescence (ED-XRF)

Energy dispersive X-ray Fluorescence (ED-XRF) spectroscopy is a powerful technique used for analysing and characterizing the sample elemental composition.

In this study, the X-ray fluorescent was used to identify the different elemental content of the samples by using the peaks energy position. Figure 3.5 shows a schematic representation of ED-XRF spectroscopy. The X-rays from the source focused on the sample through a spectral collimator and the characteristic X-rays are detected almost normally by an Amptek XR-100CR sensitive solid-state detector. The multichannel analyser separates different elemental peaks and the analysis software (MCDWIN-MCA3/ ComTek production) gives the final list of elemental contents.

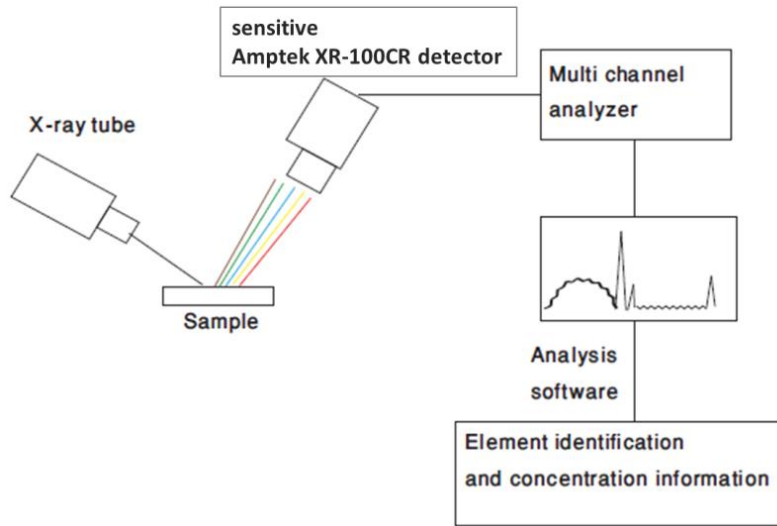


Figure 3.5: The schematic of an EDXRF Spectrometer.

3.4 X-ray Diffraction (XRD)

The X-rays of a specified wavelength incident on some powder specimen reflected forming diffraction pattern, according to the Bragg condition that is expressed by the following equation:

$$n \lambda = 2d \sin \theta \quad (3.1)$$

Where d is the spacing between reflected crystallographic planes, λ is the wavelength of the source, n is an integer and θ is called the Bragg angle of the reflected radiation.

In the present work, the structural analysis was performed by using a Rigaku Ultima VI θ - 2θ X-ray diffractometer equipped with Cu K_{α} radiation (0.154056 nm), as shown in Figure 3.6. The X-ray patterns were obtained by 2θ scan ($2\theta = 20$ - 80°) with scan step size of 0.02°



Figure 3.6: Rigaku powder diffractometer.

3.5 Diffuse Reflectance Spectroscopy (DRS)

The optical properties and energy band gap of the powder samples were studied with diffuse reflectance spectroscopy (DRS) method by using K-M equation. The spectrophotometric measurements of $R_{\text{diff}}(\lambda)$ were performed over the wavelength range 190–850 nm with Shimadzu UV-3600 double beam spectrophotometer equipped with an integrating sphere, as shown in Figure 3.7. The diffuse reflectances from the samples were measured relative to the standard reflectance from BaSO_4 white powder supplied by Shimadzu Company.

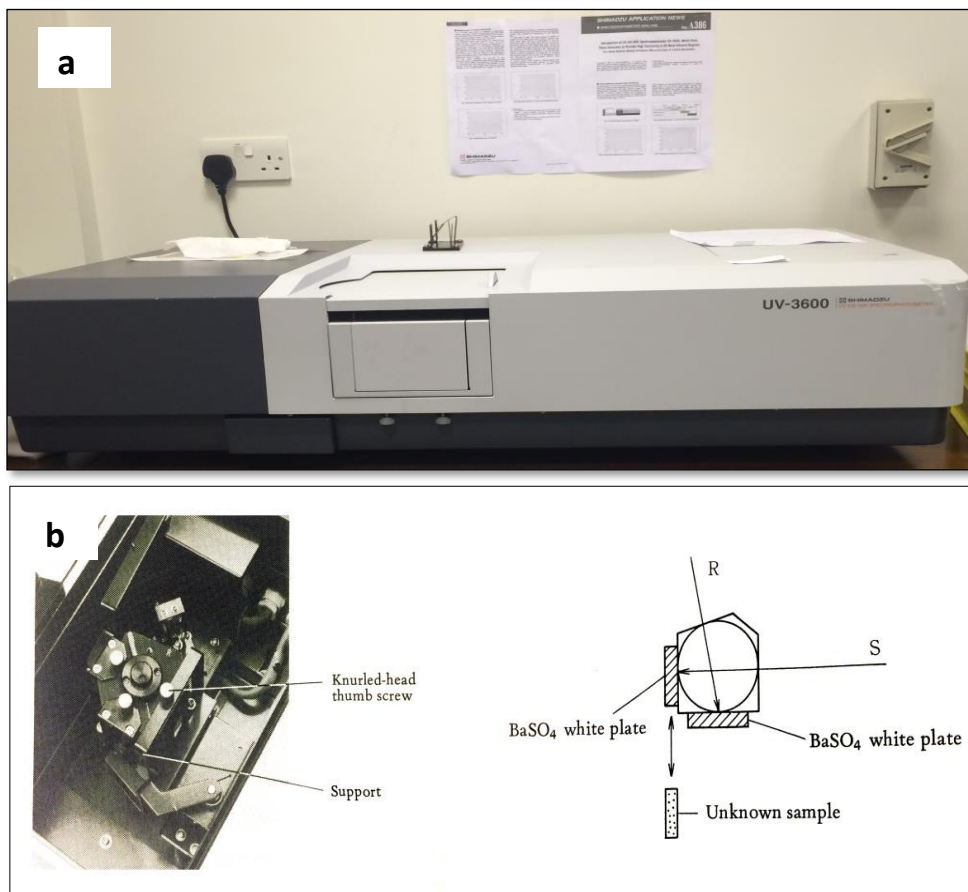


Figure3.7: **a** Shimadzu UV 3600 double beam spectrophotometer **b** Measurement setup of Diffuse Reflectance attachment to the Shimadzu UV 3600 double beam spectrophotometer.

3.6 Vibrating-Sample Magnetometer (VSM)

Magnetic characterization of the prepared samples were measured by using a vibrating sample magnetometer (VSM) type Micro-Mag Model 3900 with a sensitivity of $0.5 \mu\text{emu}$. The sample was introduced in a constant uniform external magnetic field which stimulates a magnetization in the sample. As the magnetized sample is vibrated, it introduces vibrations in the external magnetic field. Before placing the sample, the magnetometer is calibrated using a material of known

magnetization which is usually a sphere of pure nickel that gives 75.98 emu.

A set of pickup coils were arranged around the sample to measure these vibrations as shown in Figure 3.8. The Magnetization measurements performed on the sample by using a step field of 25 Oe and an averaging time of 1 s. The magnetic properties were measured at room temperature ($T = 294\text{ K}$) in the field range from + 1 to -1 T .

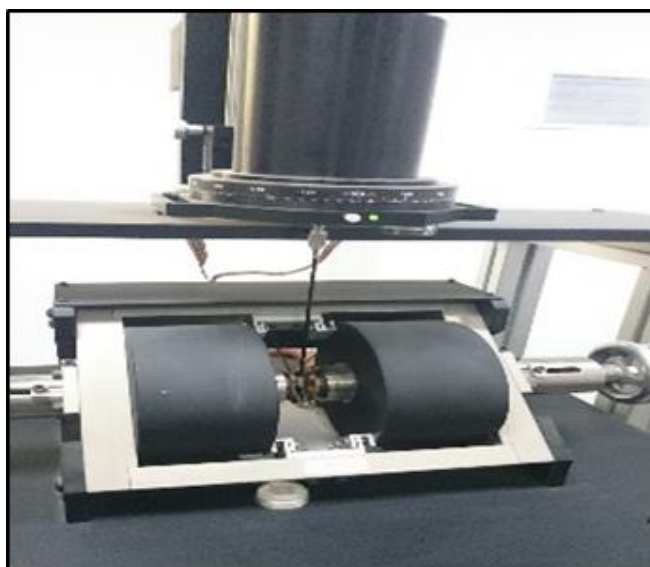


Figure 3.8 .The sample attached to a vibrating sample holder vibration along z-axis.

CHAPTER FOUR: RESULTS AND DISCUSSIONS

**4.1 Elemental content of as-synthesized (CdO:Gd:Al)
powder by X-ray Fluorescence (XRF)**

**4.2 Structural characterization by X-ray
diffractometer (XRD):**

4.2.1 Structural properties of as-synthesized powders.

4.2.2 Structural properties of hydrogenated powders.

**4.3 Optical characterization by analysis of
Diffuse reflection spectroscopy (DRS) method.**

**4.4 Magnetic properties by measured by a Vibrating-
sample magnetometer (VSM)**

4.1 Elemental Content of the As-synthesized Powder (CdO:Gd:Al) powder by X-ray Fluorescence

Fig. 4.1 demonstrates the energy-dispersive X-ray fluorescence (EDXRF) spectrum for the prepared Gd- and Al-codoped CdO pressed powder disc and a reference un-doped CdO powder disc for comparison. The spectrum reveals signals from Cd $L\alpha$ -spectrum of energy 3.17 keV, Gd $L\alpha$ and $L\beta$ – signals of energies 6.07 keV and 6.74 keV, respectively in addition to exciting radiation Cu $K\alpha$ and $K\beta$ – signals of energies 8.05 keV and 8.94 keV, respectively. Signal for the Al cannot be detected by the used set of XRF. No other signals were detected referring to the purity of the prepared samples.

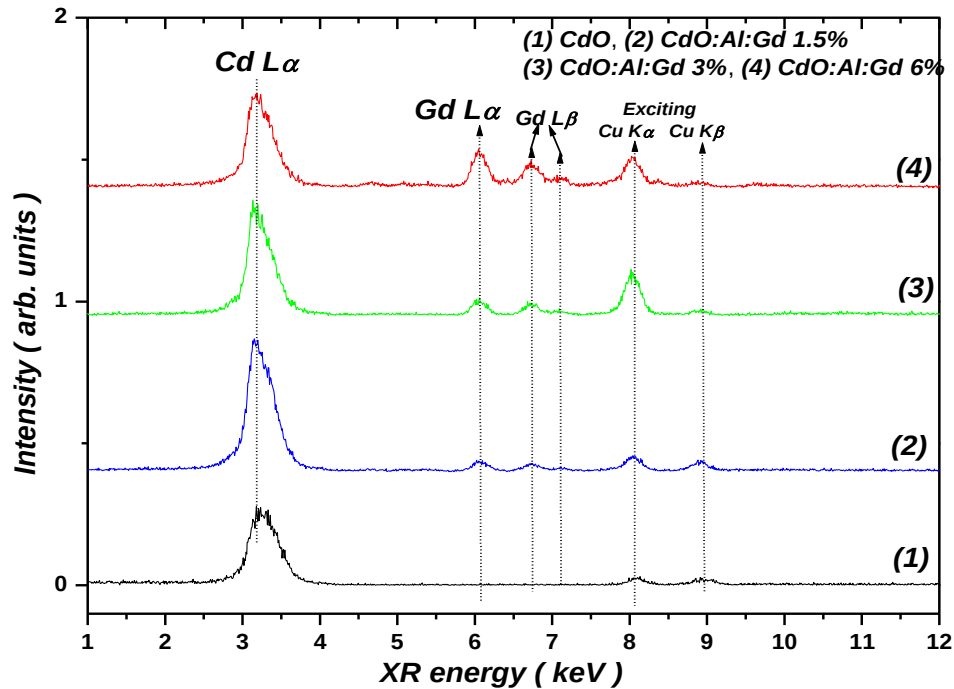


Figure 4.1: X-ray fluorescence of as-synthesized undoped and Gd- and Al-codoped CdO powder.

Table 4.1 and figure 4.2 show the dependence of the intensity ratio of L_α signals on the Gd/Cd mass content ratio of the as-synthesized powders. It can be noticed that the L_α intensity ratio increases almost linearly with the increase of the Gd % doping level.

Table 4.1: L_α intensity ratio and Gd/Cd mass content ratio (Gd % doping level) of the as-prepared CdO powders codoped with Gd and Al.

Sample	(Gd/Cd) Intensity ratio	Mass ratio
CdO:Al:Gd 1.5%	0.041	1.5%
CdO:Al:Gd 3%	0.078	3%
CdO:Al:Gd 6%	0.21	6%

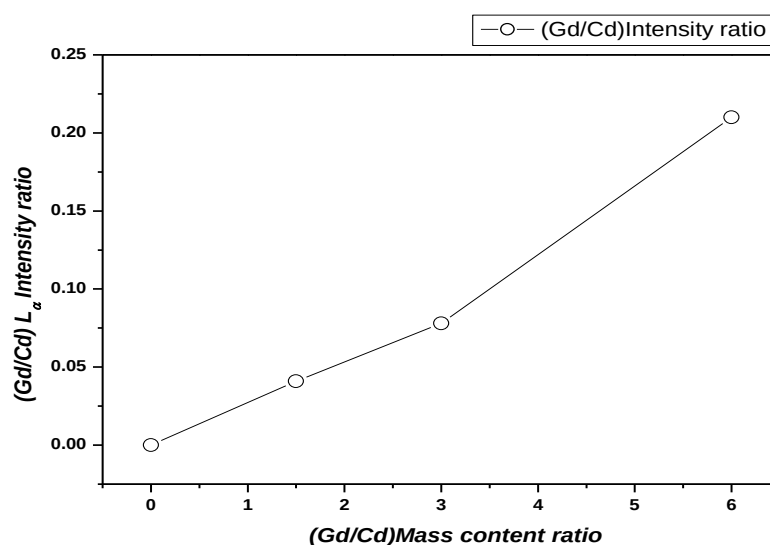


Figure 4.2: L_α intensity ratio and Gd/Cd mass content ratio relationship of the prepared CdO powders codoped

4.2 Structural characterization by X-ray diffraction

4.2.1: Structural properties of the as-synthesized powders

Fig.4.3 shows the XRD patterns of the as-synthesised Al/Gd-codoped CdO samples. The XRD of undoped CdO powder synthesised by the same procedure was depicted in Figure 3.4, for comparison. The diffraction pattern of pure, 1.5%, 3% and 6% Gd doped CdO NCs show polycrystalline in nature of cubic (Fm-3m) CdO structure. Thus, the absence of any peak from any Gd or Al related phases indicates that all the incorporated Gd and Al ions were really doped into the crystalline lattice of CdO NCs forming substitutional solid solution (SSS). This observation is important in order to explain the created magnetic properties.

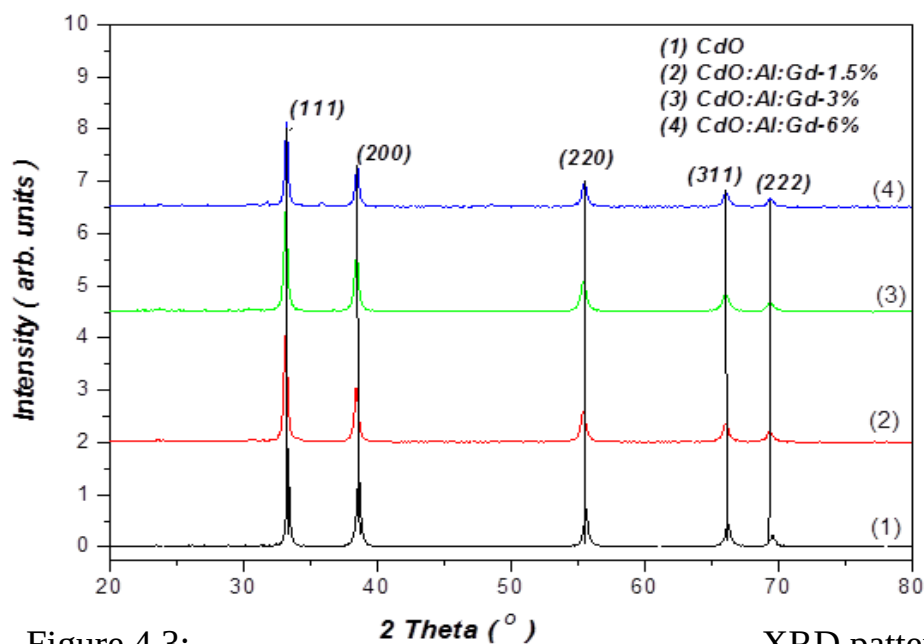


Figure 4.3: XRD patterns of the prepared un-doped and Gd/Al-codoped CdO powders.

The structural analysis including CS and strain, and lattice parameter were respectively calculated by using the Halder-Wagner and Rietveld refinement methods, which are the built-in software of the used XRD

apparatus. The results are tabulated in Table 4.2. The values of the statistical Rietveld fit parameters [R_{wp} (%) weighted profile R-factor; R_p (%) profile R-factor; R_e (%) expected R-factor; $S = R_{wp}/R_e$ and $\chi^2 = S^2$] indicate acceptable fitting as S parameter values lay between 1 and 2 (McCusker et al., 1999), which can also be noticed graphically in Figure. 4.4.

Table 4.2: Structural analysis: Crystallite size (CS in nm), microstrain ε (%), lattice parameters $a(\text{\AA})$ and $c(\text{\AA})$, $V_{\text{cell}} (\text{\AA}^3)$ and Rietveld refinement quality parameters (R_{wp} , R_p , R_e , S , and χ^2).

Sample	CS (nm)	Strain (%)	Lattice Parameter ($\text{\AA}$)	$V_{\text{Cell}} (\text{\AA}^3)$	Refinements Factors				
					$R_{wp}(\%)$	$R_p(\%)$	$R_e(\%)$	S	χ^2
CdO	41.3	0.26	$a=b=c=4.664$	101.5	16.98	13.65	11.4	1.487	2.211
CdO HH	~ 41	0.23	$a=b=c=4.694$	103.45	19.78	17.03	14.28	1.384	1.917
CdO:Al:Gd 1.5%	35	0.33	$a=b=c=4.7016$	103.93	20.66	16.78	13.53	1.525	2.325
CdO:Al:Gd 3%	34	0.38	$a=b=c=4.6916$	103.27	18.36	14.31	13.61	1.346	1.814
CdO:Al:Gd 6%	20.5	0.06	$a=b=c=4.6870$	102.96	25.64	20.69	14.3	1.790	3.206
CdO:Al:Gd 1.5%H	41.2	0.35	$a=b=c=4.697$	103.66	22.02	17.35	14.3	1.537	2.362
CdO:Al:Gd 3%H	38	0.358	$a=b=c=4.6985$	103.72	18.57	13.43	12.99	1.427	2.037
CdO:Al:Gd 6%H	31.5	0.27	$a=b=c=4.701$	103.92	13.55	10.6	11.67	1.159	1.344
CdO:Al:Gd 1.5%HH									
Cd	8.3		$a=b=2.980, c=5.619$	43.201	13.94	10.68	12.99	1.427	2.037
CdO	22.7		$a=b=c=4.706$	104.24					
CdO:Al:Gd 3%HH									
Cd	57.6		$a=b=2.9803, c=5.6202$	43.231	26.35	20.56	12.82	2.052	4.211
CdO	21.8		$a=b=c=4.698$	103.69					
CdO:Al:Gd 6%HH									
Cd	74.48		$a=b=2.9782, c=5.6162$	43.141	13.03	10.11	11.74	1.1076	1.226
CdO	33.5		$a=b=c=4.699$	103.70					

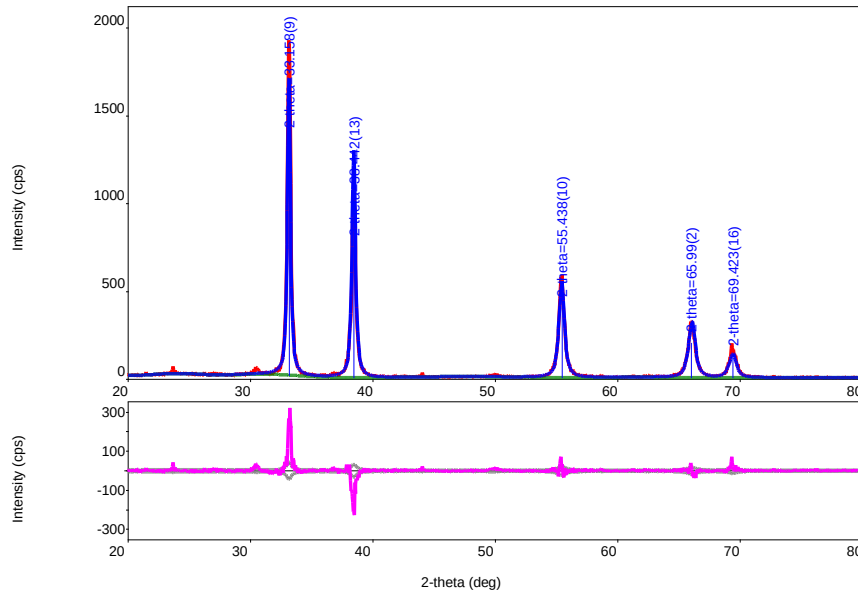


Figure 4.4: Rietveld refinements of the as-prepared CdO:Al:Gd 3% solid solutions. Experimental data; solid pink line (down): intensity difference, calculated pattern; red solid line.

The calculated lattice parameter for un-doped and codoped CdO powders is very close to their standard value in JCPDS card No. 05–0640 (0.4695 nm). However, the lattice parameter and the unit-cell volume (V_{cell}) of the host CdO have respectively decreased from 35 nm to 20.5 nm and from $103.9 \text{ \AA}^3$ to $102.9 \text{ \AA}^3$ as shown in Table 4.2 and Figure 4.5 with increasing of Gd% doping level. This can be referred to the small ionic radius of Al^{3+} and Gd^{3+} as compared to Cd^{2+} (Shannon, 1976). This proves that both Al^{3+} and Gd^{3+} ions have successfully merged into the crystalline lattice of CdO. According to the well-known Hume-Rothery rules (Kittel, n.d), the ionic radii difference should be lower than 15% in order to obtain SSS. Based on that rule; as long as the radius of Al^{3+} ions is lower than that of Cd^{2+} ions by $\sim 28\%$, Al^{3+} ions cannot form a (SSS) with Cd^{2+} . Therefore, incorporation of Al^{3+} ions by occupying interstitial sites of CdO lattice structure is most likely to occur rather than substitution of Cd ions as shown in figure 4.3. In addition, it is possible to

assume integration of Gd^{3+} ions with CdO crystal when being replaced for Cd^{2+} ions forming SSS. As a result, the radius of Gd^{3+} ions is slightly smaller than Cd^{2+} ions by only 1.2%. The substitution of Cd^{2+} ions by Gd^{3+} ions leads to disturbing charge balance of the host CdO. Consequently, the host crystal would rebalance by creation O vacancies. That what makes the unit cell volume of CdO decreases with increasing doping Gd^{3+} ions as shown in Figure 4.5.

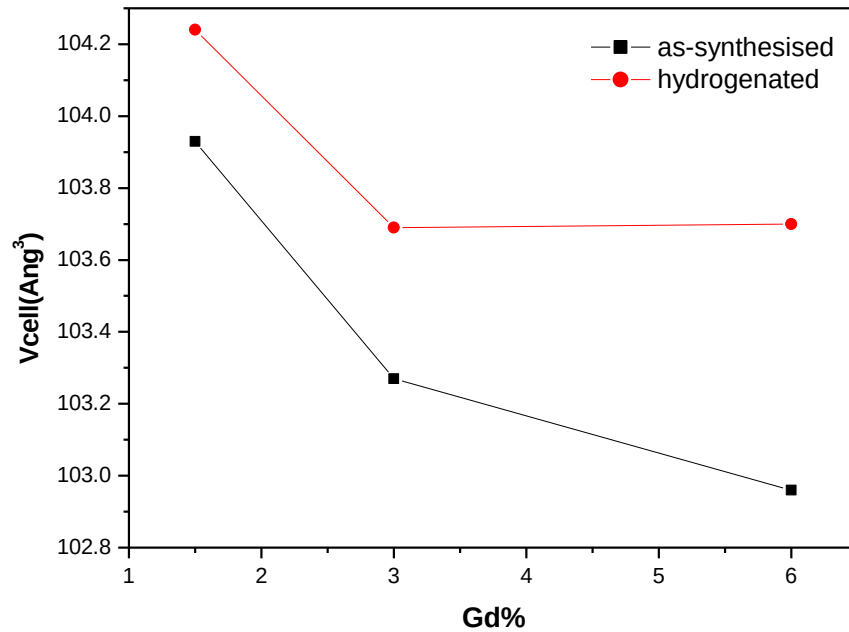


Figure 4.5: Gd doping level-dependence of the unit cell volume of host CdO for the as-synthesized and hydrogenated SSS powders.

Figure 4.6 shows the variation of the CdO NCS size with Gd% doping level. It can be seen that the average CS varied slowly upto level 3%Gd, then increases quickly to 20.5 nm at level 6%Gd due to the gradual corroid of crystallites by accumulation of added Gd on their boundaries. The hydrogenation (H) increased the CS for all doped samples except the undoped. This behaviour related to the dissociation of H_2 gas into H atoms/ions under the presence of Al and Gd dopant ions behave as “catalyst” for H_2 dissociation. Samples (HH) did not considered with data

of figure.4.6 due to the formation of Cd nanograins that affects on the calculation.

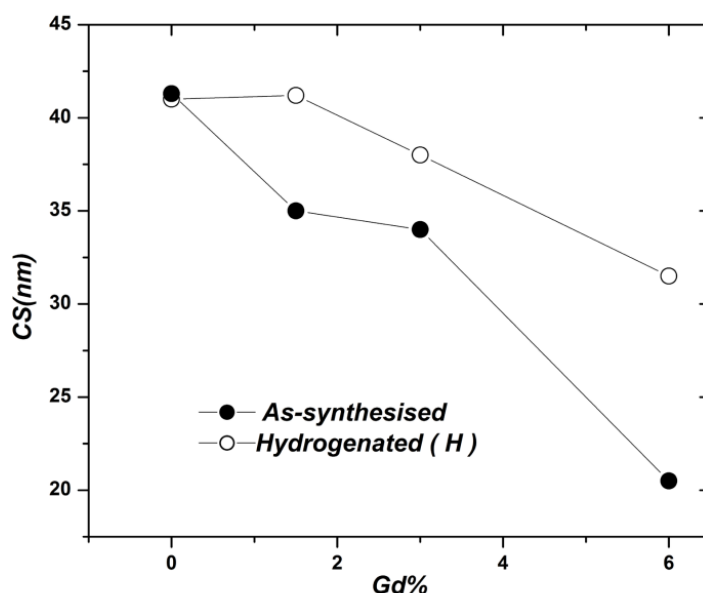


Figure 4.6: Crystallite size dependence on Gd% doping level of the as-synthesized and hydrogenated SSS powders (H)

4.2.2 Structural properties of H-annealed powders

After treating the as-synthesised samples in hydrogen atmosphere for the first time (First hydrogenation-H), the XRD pattern did not show any additional peaks raised from Al, Gd metal or their oxides, Hydride or any Al or Gd related phases, as shown in Figure 4.7. All the calculated lattice parameter of the hydrogenated samples are almost between 0.469 and 0.470 nm which is close to that value in JCPDS card No. 05-0640.

However, it was noticed the appearance of free cadmium metal (HCP) nanograins due to the hydrogenation for the second time (HH), for all the doped samples as seen in Figure 4.8. That was not found in un-doped cadmium oxide when it was treated twice with hydrogen gas as shown in

Figure 4.9. Therefore, appearance of Cd reflections indicated formation of a nano-composit mixture of CdO:Al:Gd nanograins and Cd metal nanograins .

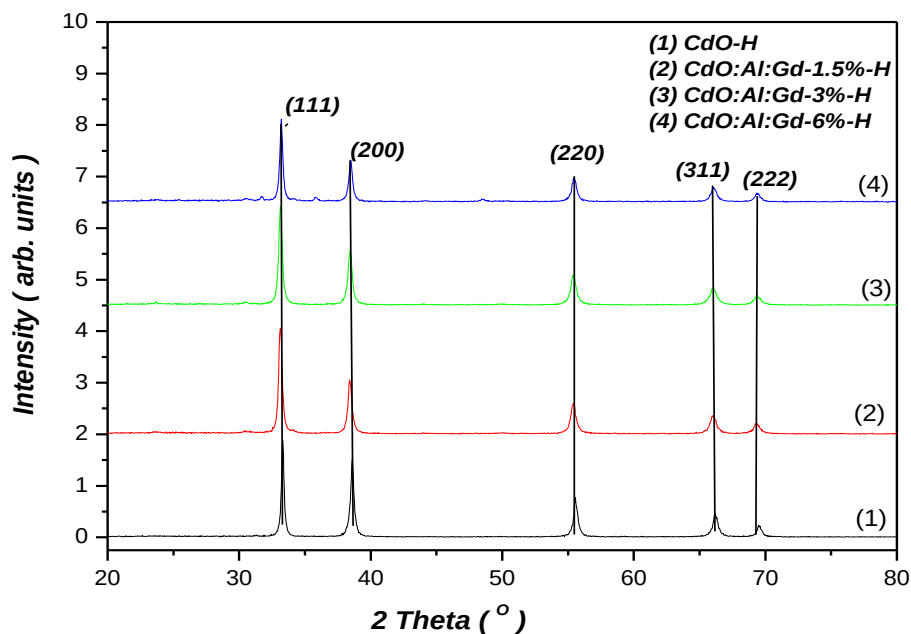


Figure 4.7.XRD patterns of un-doped and Gd and Al-doped CdO powders annealed in hydrogen atmosphere once.

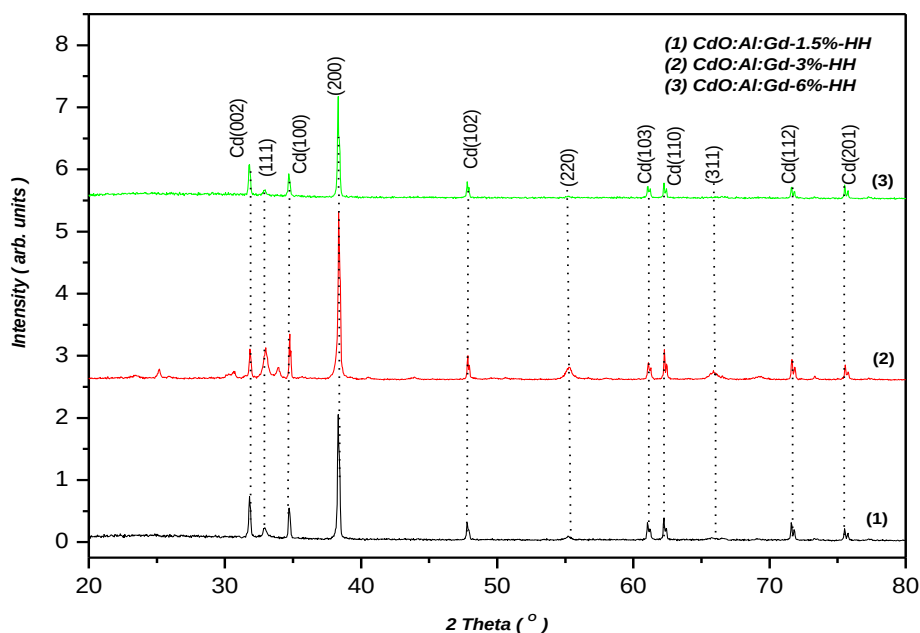


Figure 4.8.XRD patterns of un-doped and Gd and Al-doped CdO powders hydrogenated twice.

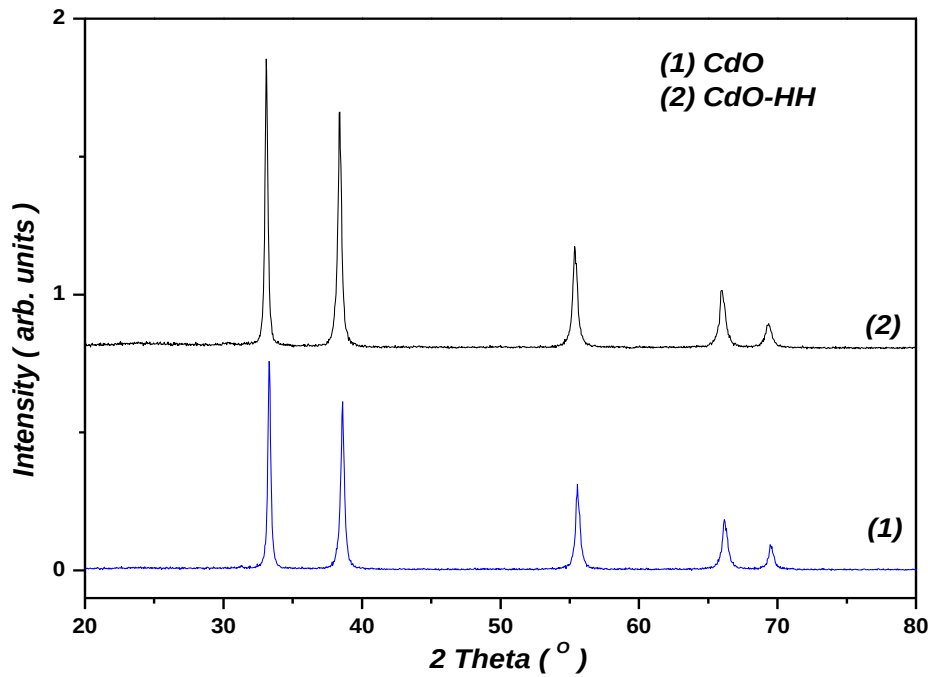


Figure 4.9. XRD patterns of un-doped CdO powders annealed in air (1) and hydrogen atmosphere twice (2).

The peaks of freed Cd nanograins were indexed according to the known hexagonal close-packed HCP (P63/mmc) structure with $a = 2.9794$ nm, $b = 2.9794$ nm, and $c = 5.6186$ nm (Winter, 2017).

As shown in table 4.1, it is clear that the second hydrogenation slightly increased the unit-cell volume of all as-synthesised samples that most likely due to the creation of O-vacancies. The following model explains the creation of O-vacancies by annealing of the samples on H_2 gas and its consequences.

As mentioned above, the result of hydrogenation of CdO:Al:Gd powders, pure Cd metal grains appeared. It is more likely to believe that H_2 molecules were dissociated into H atoms/ions by the presence of Al^{3+} and Gd^{3+} ions, which play the role of a “process catalyst”. The interaction of the H atoms/ions with structural oxygen ions, removing them from the

structure and thus forming oxygen vacancies (V_o). Moreover, that formed V_o could capture electronic charge carriers (polarons) mainly from Al dopants and hence enhances the electronic medium EMI for magnetic exchange interaction, and thus could create FM properties, which was observed experimentally (next paragraphs).

4.3 Optical characterization by diffuse reflectance spectroscopy (DRS)

The spectral diffuse reflectance $R(\lambda)$ of the synthesized powders were measured using DRS technique in the range (190-850) nm relative to standard (R_{BSO_4}) powder supplied by Shimadzu .i.e. $R(\lambda) = R_{\text{sample}} / R_{BSO_4}$, and the results are shown in Figures 4.10a, 4.11a ,4.12a and 4.13a. It can be observed that the reflectance by un-doped CdO NCs and all Al/Gd co-doped CdO NCs decreased in ultraviolet (UV) range and rapidly increased in visible (Vis) and near infrared (NIR) ranges from 550 to 850 nm.

The estimated band gap value of the as-synthesized powders given in table 4.3 were obtained by extrapolating of the linear portion of the Tauc plot $[F(R) \times E]^2$ vs. E , as shown in Figures 4.10b, 4.11b and 4.12b and 4.13b. The energy band gap for the un-doped CdO nano-powder was found to be slightly less than the values in the consistent range (2.1-2.6 eV) known for un-doped CdO films prepared by different methods (Dakhel and Al-Naser, 2016). However, with Al/Gd codoping, it was observed, within the accuracy of the Tauc method, that there was almost no net change in E_g at 0.5% Al and 1.5% Gd doping level comparing to un-doped CdO, however the band gap blueshifted with increasing of Gd% ions doping level, from (1.97 to 2.06 eV), as given in Table 4.3. These shifts refer to the incorporation Al^{3+}/Gd^{3+} ions in CdO crystalline lattice. It is known that doping with Al^{3+} redshifted the bandgap of CdO

(Maity & Chattopadhyay, 2006) due to the formation of impurity levels at the bottom of the conduction band. Meanwhile, doping of CdO with Gd^{3+} blue shifted the band gap (Gupta, Ghosh, Patel & Kahol, 2011) following Moss-Burstein phenomenon (Burstein, 1954; Moss, 1954). Therefore the net E_g shift for 1.5%Gd sample becomes almost zero.

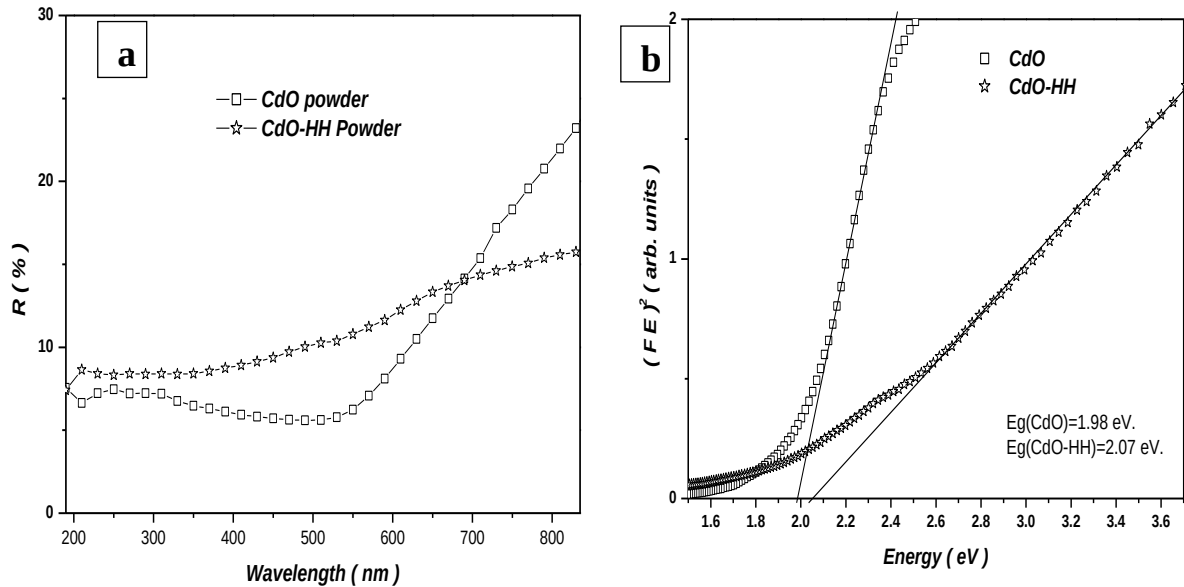


Figure 4.10: **a** The spectral diffuse reflectance, **b** $(F(R) \times E)^2$ vs. E for CdO and CdO-HH.

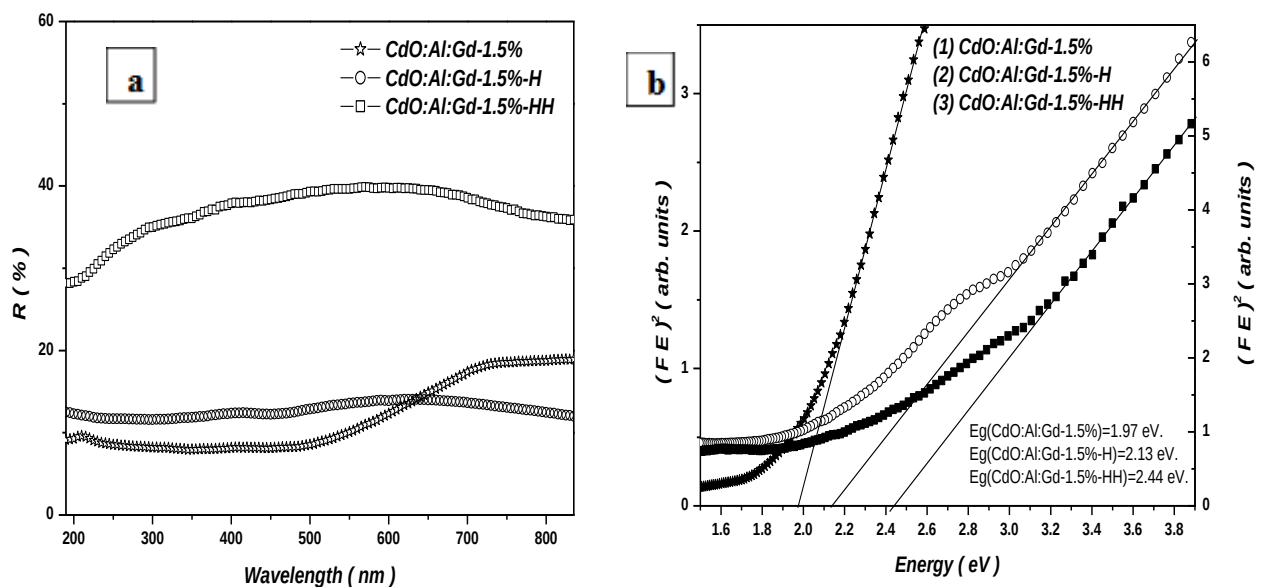


Figure 4.11: **a** The spectral diffuse reflectance, **b** $(F(R) \times E)^2$ vs. E for CdO:Al:Gd 1.5% and their hydrogenation .

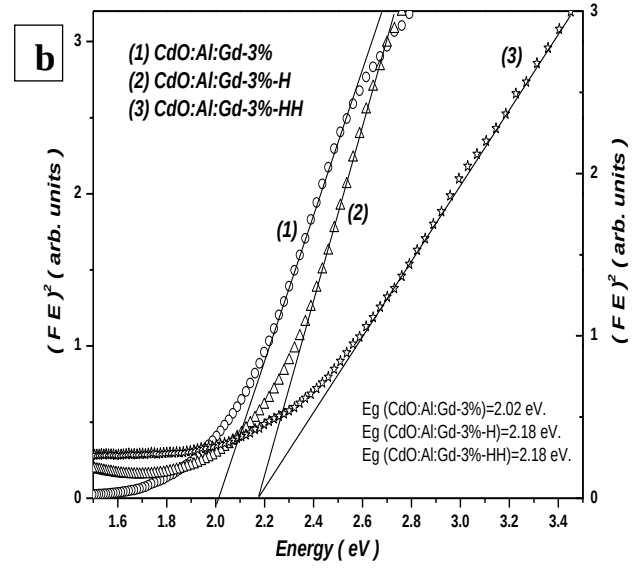
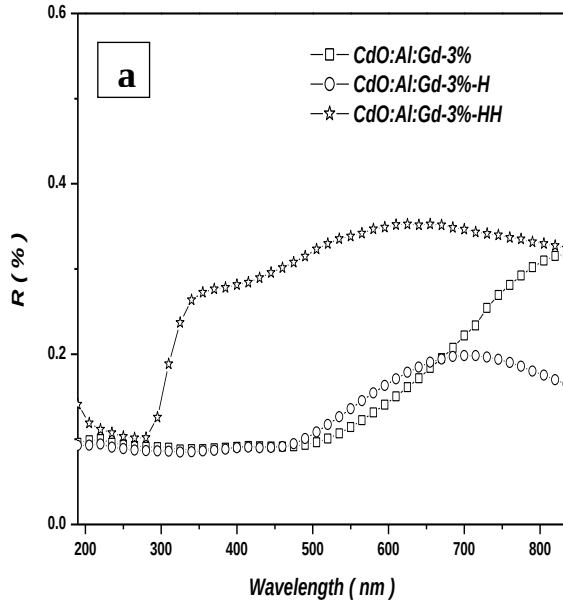


Figure 4.12: **a** The spectral diffuse reflectance, **b** $F(R) \times E)^2$ vs. E for CdO:Al:Gd 3% and their hydrogenation .

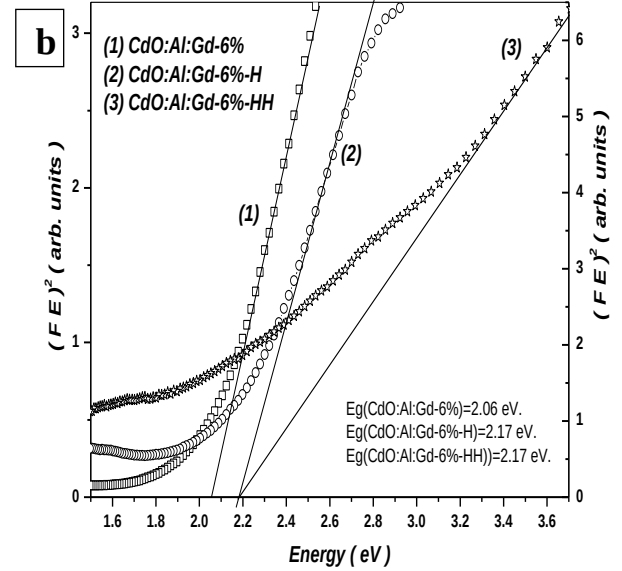
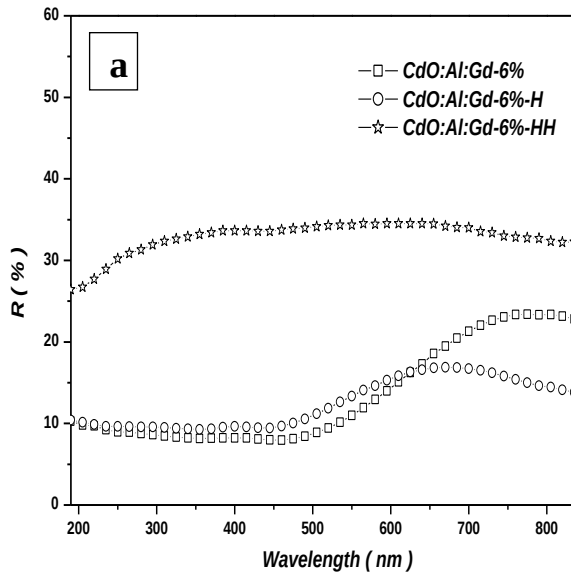


Figure 4.13: **a** The spectral diffuse reflectance, **b** $F(R) \times E)^2$ vs. E for CdO:Al:Gd 6% and their hydrogenation .

Table 4.3: Optical band gap E_g (eV) of the prepared samples.

Sample	E_g (eV)
CdO	1.98
CdO HH	2.07
CdO:Al:Gd 1.5%	1.97
CdO:Al:Gd 3%	2.02
CdO:Al:Gd 6%	2.06
CdO:Al:Gd 1.5%H	2.13
CdO:Al:Gd 3%H	2.18
CdO:Al:Gd 6%H	2.17
CdO:Al:Gd 1.5%HH	~2.44
CdO:Al:Gd 3%HH	~2.18
CdO:Al:Gd 6%HH	~2.17

However, with increasing of Gd% doping level (while Al% remained constant), a net blue shift was experimentally found as tabulated in table 4.3 and figure 4.14 which shows graphically the variation of band gap of as-synthesized samples with Gd% doping level. The values of the band gap of hydrogenated (HH) given in table 4.3 are not exact since those samples are considered as mixture of codoped CdO and nano Cd particles.

With the hydrogenation, an enhancement of the blue shift of the band gap of un-doped and codoped CdO was observed, as shown in figure 4.12b and figure 4.13b. Thus, the hydrogenation enhanced the electronic concentration since the blue shift is caused by excess in electronic concentration according to the Moss-Burstein (BM) effect, which relates

the shift of band gap ΔE_g (BM) to the change of carrier concentration, n as ΔE_g (BM) $\sim n^{2/3}$. The BM blue shift of band gap is clearly caused by increasing of carrier concentration.

Therefore, the hydrogenation of nano-crystalline CdO at low temperature (350 °C) for period (30 min) creates more conducting electron which might support the electronic medium (EMI) of the doped CdO crystal that is essential for spin-spin (**S.S**) interaction.

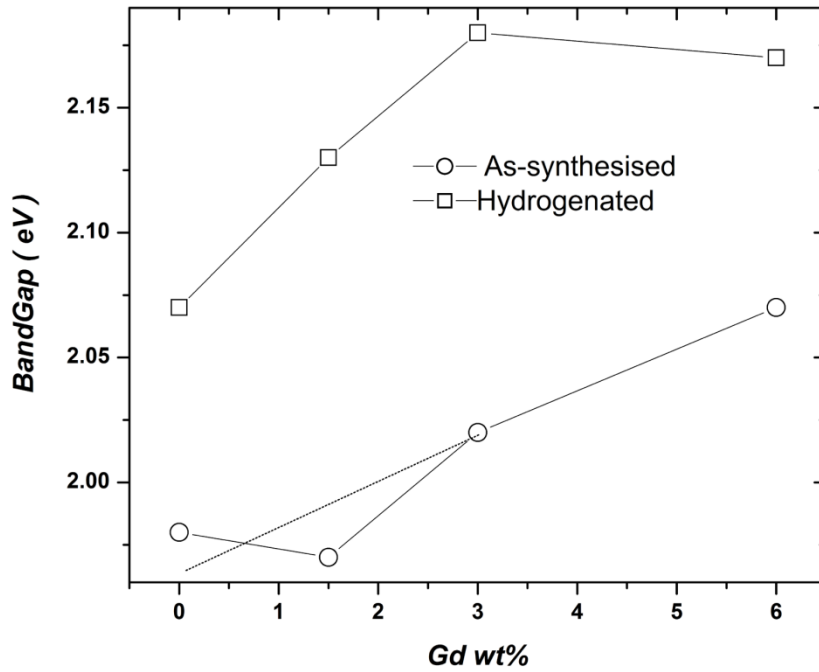


Figure.4.14: Variation of band gap of hydrogenated (H) and non-hydrogenated samples with Gd% doping level

4.4 Magnetic properties by Vibrating-sample magnetometer (VSM)

The results showed diamagnetic overlapped with weak superparamagnetic behavior for CdO NCs doped with 1.5% Gd as shown in Figure 4.15. The magnetic properties for the 3% and 6% Gd concentration in CdO NCs transformed from diamagnetic (DM) to paramagnetic (PM) are shown in Figure 4.16 and Figure 4.17. Table 4.4 shows all the magnetic parameters, which are determined from the M-H dependence, the Energy product parameter and the susceptibility per g (χ_p) for as-synthesized and hydrogenated CdO.

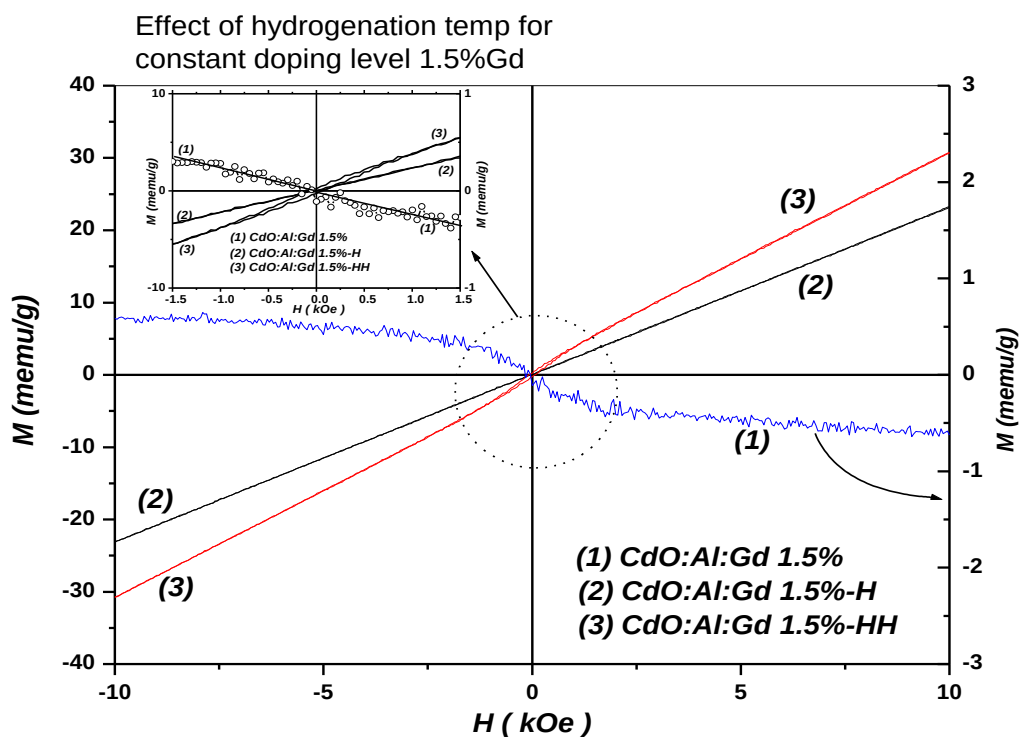


Figure 4.15: M–H dependence for the as-synthesised SSS powders at 1.5%Gd. The inset shows the effect of hydrogenation for constant doping level 1.5%Gd.

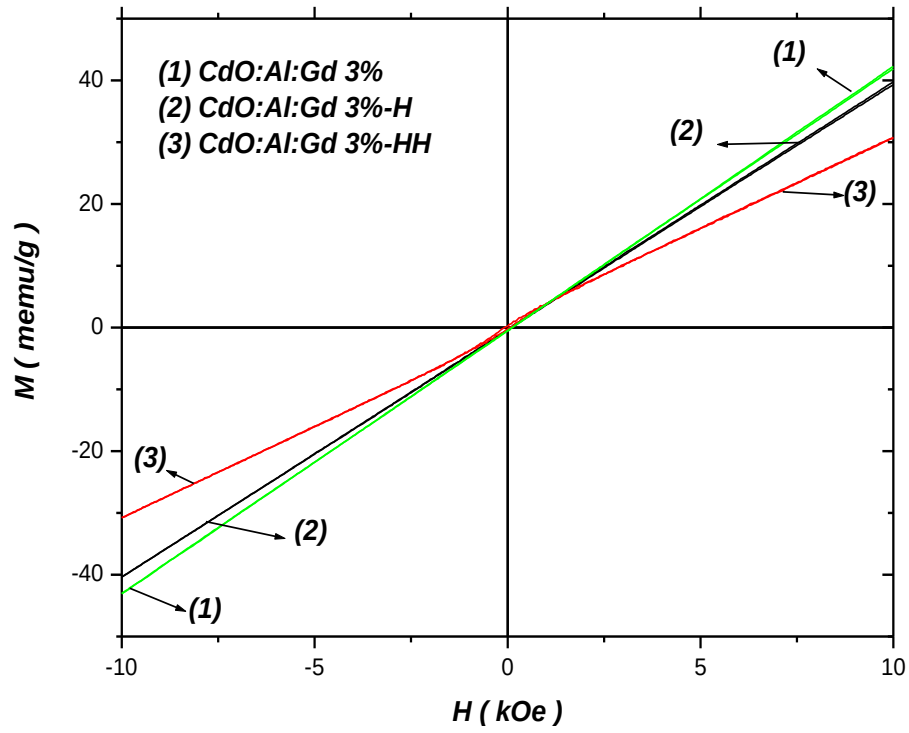


Figure 4.16. M–H dependence for the as-synthesised and hydrogenated SSS powders doped with 3%Gd.

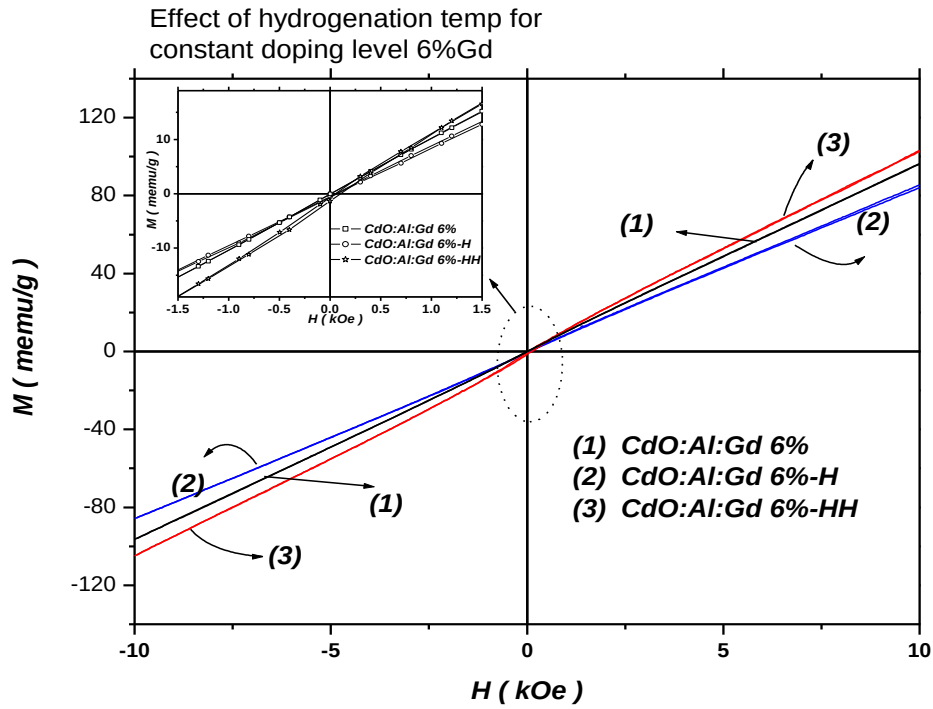


Figure 4.17: M–H dependence for the as-synthesised SSS powders at 6%Gd. The inset shows the effect of hydrogenation for constant doping level 6%Gd.

Table 4.4: Coercivity (H_c), remanence (M_r), saturation magnetization (M_s), Energy product U_m ($H_c M_r$) and susceptibility (χ_p) for as-synthesised and hydrogenated CdO powders codoped with Al and Gd.

	Sample	Behavior	H_c (Oe)	M_r (memu/g)	M_s (memu/g)	Energy product $U_m(H_c M_r)$ (m erg/g)	M_r/M_s	χ_p
Pure	CdO	Dia	-	-	-	-	-	-
	CdO HH	Dia	-	-	-	-	-	-
as-prepared	CdO:Al:Gd 1.5%	Dia	-	-	-	-	-	-
	CdO:Al:Gd 3%	Para	-	-	-	-	-	4..18E-6
	CdO:Al:Gd 6%	Para	-	-	-	-	-	9.61E-06
Hydrogenated	CdO:Al:Gd 1.5%H	Para	-	-	-	-	-	2.32E-06
	CdO:Al:Gd 3%H	Para	-	-	-	-	-	3.92E-06
	CdO:Al:Gd 6%H	Para	-	-	-	-	-	8.40E-06
Double Hydrogenated	CdO:Al:Gd 1.5%HH	Ferro	233.398	0.249	1.288	58.2	0.194	-
	CdO:Al:Gd 3%HH	Ferro	195.928	0.769	5.048	150.66	0.152	-
	CdO:Al:Gd 6%HH	Ferro	131.6	0.389	4.43	51.2	0.087	-

A linear relationship was found between χ_p and Gd% for as-synthesised samples as shown in Figure 4.18, which means that Gd^{3+} ions are mainly responsible for the observed PM properties in the CdO NCs powders.

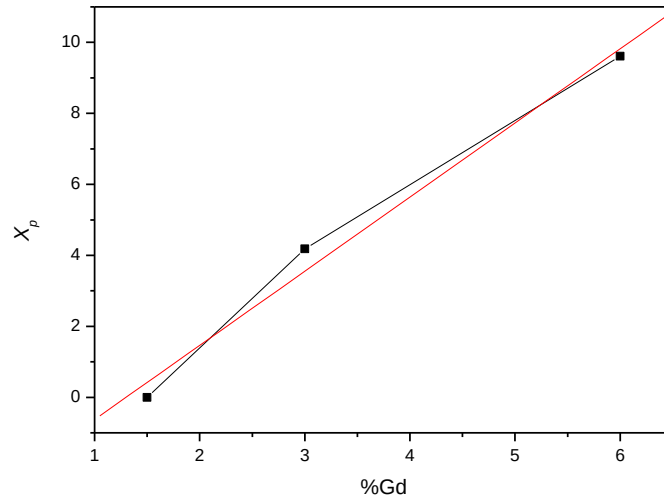


Figure 4.18: shows the linear relationship χ_p vs. Gd% for all the as-synthesized powders.

The (M-H) experimental results for the effect of the hydrogenation for 1.5%, 3% and 6% co-doped CdO nano-powders are shown in Figures 4.15, 4.16 and 4.17, respectively. In case of the hydrogenated 1.5% Gd powder, the behavior was totally converted from DM to PM as shown in Figure 4.15.

The effective magnetic moment of doped Gd ions can be estimated by applying PM Curie equation for volume susceptibility (χ_v) which is expressed in cgs units as:

$$\chi_v = D \chi_p = \frac{n_{ion} \mu^2}{3k_B T} \quad (4.1)$$

where n_{ion} is the number of doped Gd^{3+} ions per unit volume, μ is the effective magnetic moment of dopant Gd^{3+} ion, k_B is the Boltzmann

constant, D is the density of CdO and T is the working temperature. It was found that $\mu_{Gd^{3+}}$ almost equal to $\sim 8\mu_B$, where μ_B is Bohr magneton, for all the investigated powders shown Table 4.5. These values are near to the theoretical value $8\mu_B$ (Kittel & McEuen, 2015). Thus, almost all the dopant Gd^{3+} ions contribute to PM χ_p properties for all the investigated powders.

Table 4.5: Calculated value of μ for Gd^{3+} ions.

Sample	$\mu_{Gd^{3+}}(\text{erg/G})$	$\mu_{Gd^{3+}}(\mu_B)$
CdO:Al:Gd 1.5%	-	-
CdO:Al:Gd 3%	7.178×10^{-20}	7.74
CdO:Al:Gd 6%	7.64×10^{-20}	8.10
CdO:Al:Gd 1.5%H	7.544×10^{-20}	8.00
CdO:Al:Gd 3%H	6.951×10^{-20}	7.49
CdO:Al:Gd 6%H	7.19×10^{-20}	7.76

The FM component created for twice (HH) hydrogenated samples is shown in Figure 4.19.

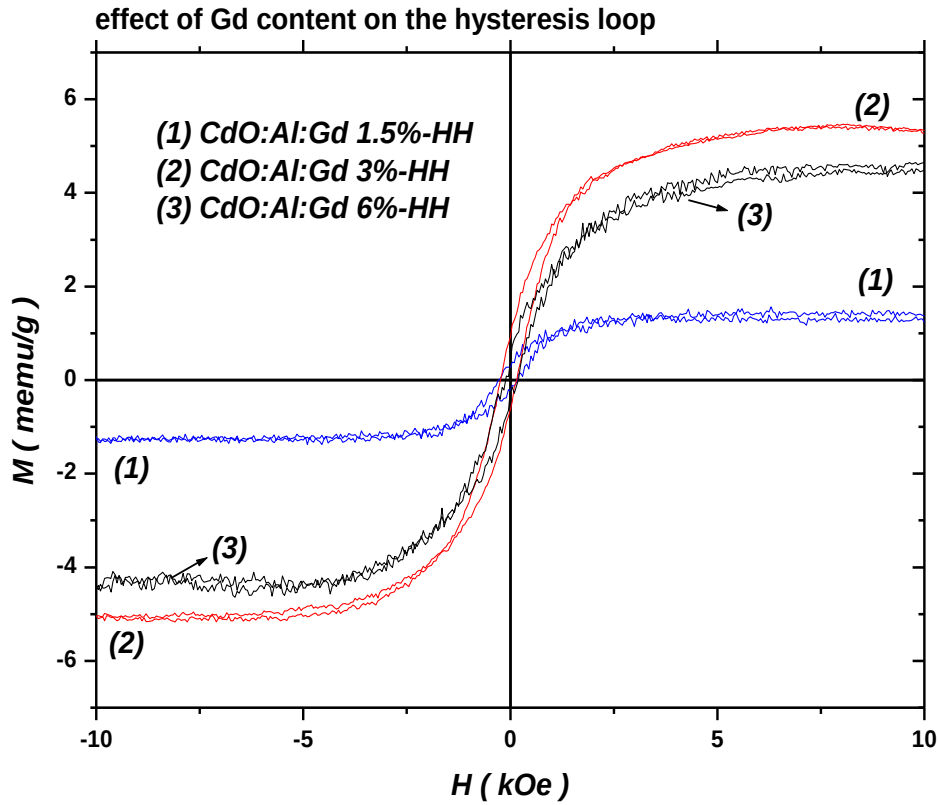


Figure 4.19: The FM component created for twice (HH) hydrogenated samples.

As shown in table 4.4, the energy product value confirms that the quality of FM in 3% Gd-HH sample of saturation magnetisation of $M_s=5.048$ memu/g better than that of 1.5%Gd-HH and 6%Gd-HH doping level .These results show the important crucial role of the EMI medium in supporting the **S.S** interaction. Therefore, the hydrogenation stimulated and developed the properties of EMI of the host CdO crystal.

Generally, the spin-spin (**S.S**) exchange interactions between dopant magnetic ions are necessary to switch on the FM behaviour. The **S.S** interaction strength depends on the average inter-dopant-ionic distances (R), in addition to the properties of the electronic medium (EMI). In addition, it was mentioned in other studies (Bergqvist et al., 2004; Seo et al., 2012; Dakhel, 2016) that in order to switch-on FM interaction, the **S.S**

exchange interaction requires that $R \leq 1.5 a$, where (a) is the lattice parameter of host medium. R could be estimated as it is the radius of a sphere around each dopant Gd^{3+} ion. For uniform distribution of Gd^{3+} dopants within the host CdO NCs, R could be estimated by $n_{Gd}V=1$, where n_{Gd} is the dopant Gd^{3+} concentration and $V = (4/3)\pi R^3$. Thus the condition $R \leq 1.5 a$ is not achieved in the present doping level, as shown in Table 4.6, which means that FM interaction either be absent or might be present very weakly. Thus, the **S.S** exchanges interaction in the present work could be generated only by hydrogenation (HH). This process prepares the EMI medium to carry the **S.S** interaction, leading to the creation of the FM properties.

Table 4.6 Calculated radius of a sphere around each dopant Gd^{3+} ion for CdO:Al:Gd powders.

Sample	$R(\text{nm})$	$1.5 a(\text{nm})$
CdO:Al:Gd 1.5%	2.40	0.70
CdO:Al:Gd 3%	1.73	0.70
CdO:Al:Gd 6%	1.37	0.70

The presence of TM ions, like Gd^{3+} as dopants acts as a catalyst for dissociation of adsorbed H_2 gas process (Pozzo and Alfe, 2009). The liberated H atoms/ions interact with structural oxygen of CdO crystal creating O-vacancies (V_O). This is necessary to develop the EMI for the Gd^{3+} - Gd^{3+} spin (**S.S**) interaction by increasing of O-vacancies in order to generate the FM. Furthermore, the O-vacancies bound some polarons

through which the **S.S** exchange interaction couples the Gd^{3+} ions and switching on long-range FM ordering.

Figure.4.20 shows graphically the data of table 4.4. Thus, the utmost created FM properties among the samples were found in host sample CdO doped with % Al and 3%Gd ions. The gradual decrease in the created FM with increasing of Gd ions doping at $\sim 6\%$ and more is attributed to the accumulation of Gd dopant on crystallite boundaries that screened doped Gd ions inside the SSS crystallites and electrostatically mutually interact to create FM. The described behavior shows the limited solubility of Gd in CdO.

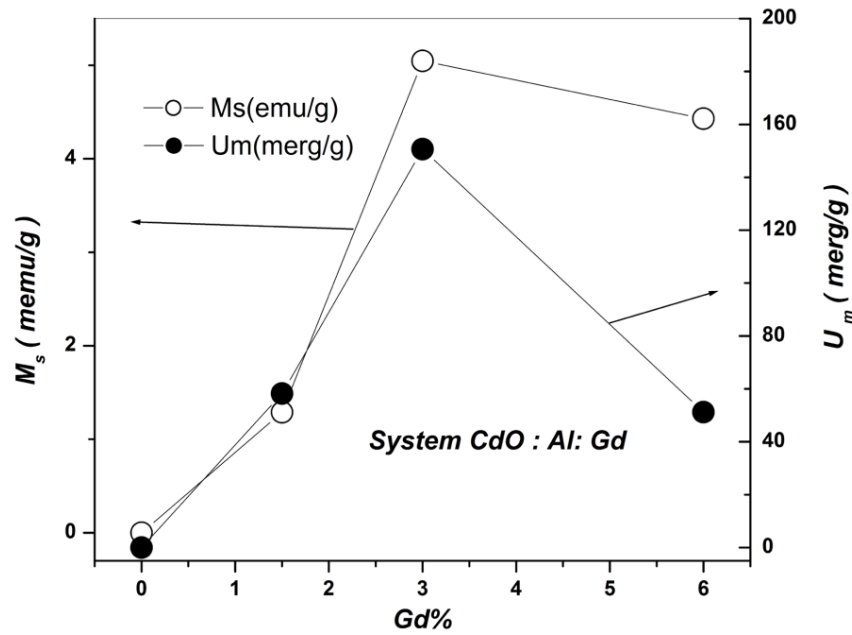


Figure.4.20: The graphic show the relationship between M_s vs. Gd% and U_m vs. Gd% for as-synthesised and hydrogenated CdO powders codoped with Al and Gd.

CHAPTER FIVE: CONCLUSION AND RECOMMENDATION

5.1 Conclusion

5.2 Recommendation

5.1 Conclusions

Gd/Al ions were successfully codoped into CdO NC lattice by thermal de-composition method followed by heat treatment. The structural study showed that CdO NCs was polycrystalline in nature and, of cubic (Fm-3m) CdO structure. This indicated that the incorporated Gd and Al ions were doped into the crystalline structure of CdO NC forming SSS. IT was concluded that due to the size effect, Al ions could occupy interstitial position of CdO, while Gd ion could substitut for crystalline Cd ions forming SSS. It was concluded that part of the incorporated ions was accumulated on the crystallite internal boundaries, due to the limited solubility of Gd in CdO.

As a directly observed result of the hydrogenation of CdO:Al:Gd powders, pure nanograins Cd metal were liberated meanwhile V_o s were created in the CdO lattice structure. The optical study showed that the band gap increased with increasing doping level, Gd^{3+} ions. Moreover, the hydrogenation enhanced the bandgap of un-doped CdO and codoped CdO reflecting the increase in the conduction electronic concentration. The result showed that doping with Gd/Al ions are important but not sufficient for the creation of RT-FM in host CdO, however it needs to enforce and enhance the necessary EMI medium for S.S interaction .The hydrogenation under some conditions (as observed in the present work) of CdO powder enhanced the electronic concentration and oxygen vacancies. This resulted in enhancement of the electronic magnetic medium to carry the spin –spin (**S.S**) interaction and create FM behavior. Thus it was proved, for the first time, the possibility of manufacturing CdO with stable RT-FM by doping and post treatment under hydrogen atmosphere, thus a new potential candidate could be used as a dilute magnetic semiconductor (DMS). Furthermore, this work open ways of

different doping procedure in order to create and apply CdO in different magneto-opto-electronic industries. Thus it was proved the possibility of preparing Gd/Al codoped CdO powders with tailored magnetic properties and becoming a potential candidate for future DMS applications.

5.2 Recommendation

Scanning electron microscope (SEM) is needed to investigate the morphology and chemical composition for pure and Al / Gd co-doped CdO powder. Also, Fourier Transform Infrared Spectroscopy (FTIR) is required to identifies the chemical bonds for all doped and hydrogenated samples.

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جامعة البحرين

قسم الفيزياء



كلية العلوم

**المغناطيسية الحديدية في درجة حرارة الغرفة لمسحوق
بلوري- نانوي من أوكسيد الكاديوم المطعم بالألومنيوم
والغادولينيوم: المعالج في جو من الهيدروجين**

مخطط بحث لاستكمال متطلبات الحصول على درجة الماجستير في الفيزياء التطبيقية

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مملكة البحرين

مارس ٢٠١٨

ملخص البحث

تم إعداد مسحوق أكسيد الكاديوم المطعم بشوارد الألمنيوم والجادلينيوم بطريقة التفكيك الحراري. تُبنت نسبة كتلة الألمنيوم/الكاديوم في هذه الدراسة في حين تم تغيير نسبة كتلة الجادلينيوم/ الكاديوم بشكل منهجي. الهدف من الدراسة الحالية هو تحضير مسحوق له خصائص مغناطيسية في درجة حرارة الغرفة، ولتحقيق هدف هذه الدراسة أضيفت للمسحوق شوارد من الألمنيوم والجادلينيوم، ووضع في جو من الهيدروجين لدراسة تأثير الشوارد على الخواص المغناطيسية.

تؤكد قياسات الإصدار الفلوري للأشعة السينية وحيود الأشعة السينية على تكوين بنية نانو - بلورية نقية للمساحيق المحضرة، وبالتالي اندماج الجادلينيوم والألمنيوم في أكسيد الكاديوم المضيف وتشكيل محلول صلب لدراسة خواصه المغناطيسية. لإجراء هذه الدراسة استخدمنا المساحيق المحضرة والمهدرجة كدالة لمحتوى نسبة شوائب الجادلينيوم. وقد لوحظ أن السلوك المغناطيسي لأكسيد الكاديوم النقي تحول من مغناطيسية مغايرة (مغناطيسية ضعيفة) إلى مغناطيسية مسايرة (ذو إنفاذية مغناطيسية)، وذلك بعد إضافة شوائب من شوارد الألمنيوم والجادلينيوم. الأهم من ذلك، فقد وجد أن العلاج في جو من الهيدروجين يحفز أكسيد الكاديوم لتشكيل معدن الكاديوم، وقد أدى هذا التحول الكلي لأن تتخذ المادة سلوكًا مغناطيسيًا حديدًا. أما بالنسبة إلى مسحوق أكسيد الكاديوم المهرج والمطعم بنسبة ٣% من الجادلينيوم، فقد ازدادت شدة حقل إزالة المغنطة، والدفق المغناطيسي المتخلف، والتمغنط الإشعاعي بنسبة 195.9 Oe، و 0.77 memu/g، و 5.1 memu/g على التوالي بالمقارنة مع ما تم إعداده.

وهكذا، ثبت لأول مرة، إمكانية تصنيع أكسيد الكاديوم المُتَّصف بمغناطيسية مستقرة عند درجة حرارة الغرفة، وذلك عن طريق التطعيم بالشوائب والعلاج في جو من الهيدروجين، وبالتالي يكون أكسيد الكاديوم مادة مرشحة محتملة جديدة يمكن استخدامها كشبه موصل مغناطيسي مخفف.