Chapter IV: Changes in structural, optical & magnetic properties of Cadmium Oxide nanoparticles induced by annealing and doping
4.1 Enhanced visible luminescence and modification in morphological properties of cadmium oxide nanoparticles induced by annealing

Cadmium oxide (CdO) nanoparticles are synthesized by a simple sol-gel synthesis method as described in section 2.2.1 of chapter II. They showed luminescence properties in visible region of electromagnetic spectrum. Both blue and green emissions were observed in PL spectra. Structural, optical and electrical properties were investigated by changing annealing temperature of the samples. Changes in luminescence intensity due to cadmium interstitial and oxygen vacancy defects of nanoparticles were realized when these particles were annealed at three different temperatures. XRD confirmed annealing induced changes in morphological properties. A good correlation between all the experimental results was obtained.

4.1.1 Diffuse reflectance spectroscopy

![Diffuse reflectance spectra](image)

**Figure 4.1:** Diffuse reflectance spectra of CdO nanoparticles annealed at three different temperatures
Chapter IV

CdO nanoparticles are synthesized by sol-gel method as explained in section 2.2.1 of chapter II. These nanoparticles are annealed at three different temperatures 400 °C, 600 °C and 800 °C. Comparison of diffuse reflectance spectra of these powder nanoparticles are shown in the above Figure 4.1. Figure 4.2 (a) and (b) are Tauc’s plots of all three samples derived from using Kubelka-Munk function $F(R)$ where $F(R)=(1-R)^2/2R$, $R$ is the reflectance in percentage [1-3]. Figure 4.2 (a) is the Tauc’s for calculation of direct band gap CdO nanoparticles and Figure 4.2 (b) is for indirect band gap.

Figure 4.2 (a): Tauc’s plot for determination of direct band gap of CdO nanoparticles

![Figure 4.2 (a)](image1)

Figure 4.2 (b): Tauc’s plot for determination of indirect band gap of CdO nanoparticles

![Figure 4.2 (b)](image2)

Urbach Energy is calculated from $F(R)$ vs $h\nu$ plot using the relation,

$\alpha(E) = \alpha_0 \exp(E-E_g)/E_0$

where $E_0$ is the characteristic width of the absorption edge called Urbach parameter, $E_g$ is the optical band gap [4]. Figure 4.3 is the Urbach energy plot for all the three samples.
Chapter IV

Calculated values of Urbach energies and band gaps are summarized in table 4.1. It is seen that direct band gap (DBG) increases with increase in annealing temperature while indirect band gap (IBG) decreases. Urbach energy also decreases with increase in annealing temperature. Increase in direct band gap and decrease in indirect band gap signifies that total defect states in the system decreased with increase in annealing temperature. Since Urbach energy is a measure of defects in the system and so decrease in Urbach energy implies that number of defects in the system decrease with increase in annealing temperature.

**Figure 4.3**: ln [F(R)] versus incident photon energy hν for CdO nanoparticles annealed at three different temperatures

**TABLE 4.1**: Comparison of direct band gap, indirect band gap and Urbach energy

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Direct Band gap (DBG), $E_{DBG}$ eV</th>
<th>Indirect Band gap (IBG), $E_{IBG}$ eV</th>
<th>Urbach Energy, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>2.8</td>
<td>1.81</td>
<td>0.94</td>
</tr>
<tr>
<td>600</td>
<td>3.08</td>
<td>1.74</td>
<td>0.70</td>
</tr>
<tr>
<td>800</td>
<td>3.24</td>
<td>1.19</td>
<td>0.69</td>
</tr>
</tbody>
</table>
4.1.2 Photoluminescence spectroscopy

PL spectra are shown in Figure 4.4 (A) and (B). Figure 4.4 (A) is the PL spectroscopy of CdO nanoparticle annealed at 400 °C and Figure 4.4 (B) is the comparison of PL spectra of CdO nanoparticles annealed at three different temperatures.

![Figure 4.4: (A) PL spectroscopy of CdO nanoparticle and (B) Comparison of PL spectra of CdO nanoparticles annealed at three different temperatures](image)

From PL spectra (Figure 4.4 (A)) of CdO nanoparticles annealed at 400 °C, it was found that the green emitting peak is actually composed of two peaks. The deconvoluted green peak is shown in inset. PL spectra of CdO nanoparticles have both green and blue emissions which are results of emissions from oxygen vacancy and interstitial vacancies [5]. In a crystal a certain number of defects always present, because entropy is increased by the presence of disorder in the structure [6]. Oxygen vacancies create deep levels and Cd-interstitials are shallow donors in CdO nanoparticles. Cd-interstitials are Frenkel type defects. These defects can move outward. Let us consider blue and green peaks of 400, samples annealed at 600 and 800 °C as  \( B_1, B_2, B_3 \) and \( G_1, G_2, G_3 \) respectively. Then the ratio of the intensity of the peaks are \( G_1/ G_2=0.54, G_1/ G_3=1.15, B_1/ B_2=0.44, B_1/ B_3=0.30 \). In Figure 4.4 (A), green peak as stated above consists of two peaks. This may be ascribed to emission from two different levels of oxygen vacancy defect states. From Figure 4.4 (B), it was found that annealing slightly red-shifted the emission peak positions for samples annealed at 600 °C and 800 °C. Red shifting can be ascribed to increase in particle size. Intensity of blue emitting peak of 600 °C sample was increased to a greater extent. But it was decreased for 800 °C sample than 400 °C sample. Intensity
of Green peak of both 600 °C and 800 °C samples increased than that of 400 °C. This is because annealing at 600 °C increases the number of Cd- interstitial vacancies by providing enough ionization energy. At this temperature Cd-interstitial vacancies, which are Frenkel defects get enough thermal energy to diffuse through the crystal and go to the surface which in turn increases blue peak intensity. But these defects are unstable in comparison to oxygen vacancy defects. At high temperature i.e. at 800 °C oxygen vacancies predominate. It may be possible that at 800 °C, Cd-interstitials get oxidized. Hence intensity of green peak of the samples increased while blue peak decreased. Because at this temperature possibility of electrons to jump down to the oxygen vacancy levels increases as now there are lesser number of Cd-interstitial defects within band gap.

4.1.3 X-ray diffraction studies

Morphological properties were studied by XRD. XRD studies have been done to find the crystal structure as shown in Figure 4.5. From Williamson-Hall plot as shown in Figure 4.6, crystallite size and strain were calculated [7]. Lattice parameter of CdO samples are calculated by using the Nelson–Riley Parameter [8] given by,

\[
\text{NRF} = \frac{1}{2} \left[ \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right]
\]

where \( \theta \) = Bragg angle. By extrapolating the lines to NRF=0, the true lattice parameter is obtained as shown in Figure 4.7.

![Figure 4.5: XRD pattern of CdO nanoparticles annealed at different temperatures](image-url)
Comparison between lattice constant, crystallite size, interplanar distance and strain of the nanoparticles are shown in TABLE 4.2. Lattice constant and interplanar distance of the nanoparticles continues to decrease with increase in annealing temperature. Although crystallite size first increases then slightly decrease with temperature. Change in lattice constant may be due to change in particle size with annealing. Annealing leads to change in number of oxygen vacancies or defects in the system which in turn changes the lattice constant, interplanar distance and strain in the nanoparticles.
**TABLE 4.2:** Comparison between lattice constant, Interplanar spacing, Crystallite size & Strain

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Lattice constant, Å</th>
<th>Interplanar spacing, d nm</th>
<th>Crystallite Size, nm</th>
<th>Strain×10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>4.8</td>
<td>0.34</td>
<td>24</td>
<td>4.68</td>
</tr>
<tr>
<td>600</td>
<td>4.71</td>
<td>0.33</td>
<td>37</td>
<td>4.11</td>
</tr>
<tr>
<td>800</td>
<td>4.38</td>
<td>0.31</td>
<td>31</td>
<td>-10.87</td>
</tr>
</tbody>
</table>

**4.1.4 I-V measurements**

I-V measurements of the samples were done by using a Keithley electrometer automatic system. Pellets were made from all the three samples and conductivity measurements were taken after making contact with silver paste. I-V curve shows linear relationship showing the contact to be Ohmic. The electrical conductivity of the samples are measured by using the following relation, \( \Omega = l/A \frac{dl}{dV} \) where \( l \) is the thickness of the sample and \( A \) is the area of the sample. Slope of the graph (Figure 4.8) gives \( (dl/dV) \) [9]. Conductivities of all the samples are given in table 4.3. Conductivities of the CdO nanoparticles for the samples gradually increase with increase in annealing temperature as shown in Figure 4.8. This type of behavior is expected for n-type intrinsic semiconductors.
It was seen that a certain amount of defects were present in the system. Here, annealing leads to increase in oxygen vacancies in the CdO nanoparticles. These oxygen vacancies capture electrons forming $V^+$ centres. In electrical conductivity, electrons trapped in oxygen vacancies also contribute. As the temperature of the samples was increased trapped electrons get sufficient thermal energy and go to the conduction band and become free electrons. So oxygen vacancies greatly contribute to electrical conductivity. With increase in annealing temperature amorphous phase in the nanoparticles decreases and crystallite size increases. Also, scattering in grain boundary is reduced with increase in annealing temperature. Hence conductivity increases.

**Figure 4.8:** Current vs Voltage plot of CdO nanoparticles
4.1.5 Hall-effect

The Lorentz force law is given by, \( F = q(E + v \times B) \). This equation states that a force (F) will be exerted when a magnetic field (B) intersects a moving charge (q) with velocity \( v \) as shown in Figure 4.9. Therefore, if a current (I) is run through the sample (palette) and a magnetic field is generated perpendicular to the current, then a force will occur on electrons moving through the material \([10]\). This will generate a potential perpendicular to both the current and the field, known as the Hall Voltage (\( V_H \), Hall, E. H.1879), defined by \( V_H = -IB/de \) where \( d \) is the thickness of the strip, \( n \) is the density of charge carriers, and \( e \) is the charge of an electron. Given this, \( n \) is calculated by \( n = -IB/deV_H \). Hall co-efficient, \( R_H = 1/nq \).

![Figure 4.9: Schematic diagram of Hall-effect](image)

Measurements were taken by a standard laboratory set up where contacts are provided by silver paint. From the slope of the graph between Hall voltage and magnetic field gives Hall co-efficient from which charge concentration can be calculated. Hall voltage versus magnetic fields graphs are shown in Figure 4.10. Hall co-efficient and charge concentration of the samples are given in table 4.4.

![Figure 4.10: Hall Voltage vs Magnetic field of all three CdO nanoparticle samples](image)
N-type electrical conductivity in CdO is due to Cd-interstitials and oxygen vacancies. With gradual increase in temperature conductivity increases due to increase in number of available free electrons in conduction band. With increase in annealing temperature potential barrier also decreases. Hence charge density also increases as it was found in Hall Effect measurements.

### 4.2 Optical and magnetic properties of Mn doped CdO nanoparticles

Transition metal Mn doping into CdO nanoparticles is especially interesting as doping of CdO gives rise to the variation in the energy band gap, carrier concentration and defects which in turn gives rise to changes in optical and magnetic properties. Main motivation of this work is to study optical and magnetic properties of Mn doped CdO nanostructures. Pristine and Mn doped CdO nanoparticles are synthesized by sol-gel method as explained in section 2.2.2 of chapter II. HR-TEM images of Mn doped CdO nanoparticles are shown in Figure 2.7 (A) of Chapter II where particle agglomeration was seen. This is
because surfactants are not used for preparing CdO nanoparticles. EDX (Figure 2.7 (C)) confirms the presence of Mn, cadmium and oxygen. Selected area electron diffraction (SAED, Figure 2.7 (B)), was also taken to confirm crystalline nature.

4.2.1 X-Ray diffraction Studies

XRD pattern for pristine and doped CdO nanoparticles are shown in the Figure 4.11. Williamson-Hall for calculation of crystallite size and strain generated in the nanoparticles is shown in Figure 4.12 (A, B, C and D). Lattice parameter of CdO samples are calculated by using the Nelson–Riley Parameter given in section 4.1.3. By extrapolating the lines to NRF=0, the true lattice parameter is obtained as shown in Figure 4.13 (A, B, C, D). Comparison between crystallite size, strain, interplanar distance and lattice constant of the nanoparticles are shown in TABLE 4.5.

![Figure 4.11: Comparison of XRD studies](image)
Chapter IV

4.12

Figure 4.12: Williamson-Hall plot of pristine and Mn doped CdO nanoparticles

Figure 4.13: Nelson-Riley plot of pristine and Mn doped CdO nanoparticles

4.12
TABLE 4.5: Comparison of crystallite size, strain, interplanar distance and lattice constant

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Crystallite size, nm</th>
<th>Strain×10^{-3}</th>
<th>Interplanar distance, nm</th>
<th>Lattice constant Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 %</td>
<td>5</td>
<td>4.68</td>
<td>0.34</td>
<td>4.8</td>
</tr>
<tr>
<td>1 %</td>
<td>5</td>
<td>5.44</td>
<td>0.19</td>
<td>4.8</td>
</tr>
<tr>
<td>2.5 %</td>
<td>4</td>
<td>4.61</td>
<td>0.18</td>
<td>4.9</td>
</tr>
<tr>
<td>5 %</td>
<td>4</td>
<td>5.23</td>
<td>0.19</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Crystallite size of the nanoparticles does not change much with doping. Strain in the nanoparticles is highest for 1 % doping. Interplanar distance decreases than that for pristine nanoparticles. Crystallite size is almost constant for all the doping concentrations and so also lattice constants as calculated from Nelson-Riley plot.

4.2.2 Diffuse reflectance and photoluminescence spectroscopy of pristine and Mn doped CdO nanoparticles

Tauc’s plots are drawn in a similar fashion as explained in section 4.1. Figure 4.14 shows comparison of diffuse reflectance spectra of the samples. Figure 4.15 (A, B, C and D) are Tauc’s plots for direct band gap of pristine and doped CdO nanoparticles. Since Mn^{2+} has no spin allowed ligand field transitions, only the transitions for CdO were observed in the F(R) versus energy curves for all the doping concentrations.
Chapter IV

4.14

Figure 4.14: Diffuse reflectance spectra of pristine and Mn doped CdO nanoparticles

Figure 4.15: Tauc’s plot for pristine and Mn doped CdO nanoparticles

Band gaps of the pristine and doped CdO nanoparticles calculated by Tauc’s plot show that it decreases with increase in doping concentration. Instead of ideal direct band–edge
absorption, an exponential tail in the absorption spectra was found which is called Urbach tail as explained in section 4.1. Defect states are formed as an intermediate state in the band gap of CdO. These defect states create a tail extending from the lower of conduction band to band gap. These states are very near to the valence band and spread the valence band edge deep inside the gap. Therefore, on both sides of the valence band maximum and conduction band minimum, an energy tail is formed. This defect tail is known as the Urbach tail [11]. The energy associated with this defect tail is referred to as Urbach energy. Dopant impurities as well as other structural imperfections for example defects such as oxygen vacancy, interstitial vacancy etc introduce lattice disorder. So, Urbach energy is used to characterize the degree of disorderness in the nanoparticles. Urbach energy was calculated using the relation given in section 4.1.1. Figure 4.16 (A, B, C and D) is the Urbach energy plot for the samples. Calculated values of Urbach energy and band gaps are summarized in table 4.16.

Figure 4.16: Urbach energy plot for pristine and Mn doped CdO nanoparticles
TABLE 4.6: Table for Bandgap and Urbach energy of pristine and Mn doped CdO nanoparticles

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Band gap eV</th>
<th>Urbach Energy eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 %</td>
<td>2.8</td>
<td>0.10</td>
</tr>
<tr>
<td>1 %</td>
<td>2.68</td>
<td>0.13</td>
</tr>
<tr>
<td>2.5 %</td>
<td>2.08</td>
<td>0.19</td>
</tr>
<tr>
<td>5 %</td>
<td>1.9</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Band gap of the nanoparticles decreases with increase in doping concentration. Decrease in band gap is may be due to trapping of Mn atoms at the grain boundary which leads to the introduction of Mn defect states within the forbidden gap. With increase in Mn concentration density of these Mn induced defect states increases, leading to the observed decrease of band gap. Urbach energy which is a measure of disorderness in the nanoparticles is higher for 1 % and 2.5 % Mn doped CdO nanoparticles than 0 %. But for 5 % Mn doped samples Urbach energy decreases than 0 % doping.

Figure 4.17: Normalized PL spectra of pristine and Mn doped CdO nanoparticles

Normalized PL spectra of pristine and Mn doped CdO nanoparticles are shown in Figure 4.17. It is seen that PL intensity decreases with increase in doping concentration. This
partial quenching in PL intensity may be due to various nonradiative processes like Auger recombination. Strong carrier to carrier interactions lead to Auger nonradiative process. Rather than releasing the energy of recombination as a photon or phonon, the excess energy is transferred to another electron known as Auger electron. The Auger electron loses its surplus energy by creation of phonon. The Auger recombination process involves two electrons and a hole in the conduction band and valence band, respectively. For 1 % doping intensity is higher than that for pristine CdO. This can happen only if the dopants are properly incorporated in the host lattice. PL spectra have both blue and green emissions which are results of emissions from interstitial vacancies and oxygen vacancies. And green emitting peak is actually composed of two peaks due to two different types of oxygen vacancies [12].

### 4.2.3 Electron paramagnetic resonance spectroscopy (EPR)

EPR is used at the microscopic level to get information about the oxidation state, lattice defects, color centres, site occupancy and magnetic phases in the host semiconductor lattice. This technique is based on the microwave absorption of unpaired electron spins in presence of an external magnetic field. EPR studies of powder of CdO nanoparticles formed at high temperature provide information about the conduction electrons, together with Cd$^{+}$ ions. Bulk CdO is a general non-stoichiometric n-type semiconductor. When it is in nano size range its properties change from Bulk. Non-stoichiometric CdO nanoparticles show asymmetric EPR signal. On the basis of other already reported results, signals with $g = 2.046686$ and $g = 2.202907$ were assigned to conduction band electrons, and to Cd$^{+}$ ions on the site of Cd$^{2+}$ in pristine CdO nanoparticles [13-15]. Cd$^{+}$ ions arise from polaronic self-trapping of electrons introduced by oxygen deficiency at Cd sites to generate localized $5s^1$ states. In ionic solids, single electrons can produce localized lattice distortions, resulting from their electrostatic interaction with neighboring ions. This type of distortion accompanies the electron as it moves through the lattice, and the result is known as polaron.
EPR spectra of pristine and Mn doped CdO nanoparticles are shown in Figure 4.18. The electronic configuration of \( \text{Mn}^{2+} \) is \( 3d^5 \) and electronic ground state is \( ^6S_{5/2} \) as the spin of \( \text{Mn}^{2+} \) is \( S=5/2 \). The energy level of electrons under an external field is again split into six lines by magnetic field produced by the nuclear spin states giving sextet of hyperfine line [16]. As the concentration of \( \text{Mn}^{2+} \) increases from 1 % to 5 %, sextet of hyperfine lines disappears and the peak broadens. Dipolar interaction between \( \text{Mn}^{2+} \)-\( \text{Mn}^{2+} \) is responsible for this EPR broadening effect [17]. No \( \text{Cd}^{+} \) related EPR signal is seen here as sextet of hyperfine lines overlaps the EPR signal due to \( \text{Cd}^{+} \) ions.

4.2.4 Origin of room temperature ferromagnetism

Magnetic hysteresis loops for the samples with three levels of Mn doping from SQUID measurements are shown in Figure 4.19. The magnetization versus magnetic field loops at room temperature exhibit coercive filed and saturation magnetization of approximately 255, 252, 230 Oe and 0.22, 0.13, 0.12 emu/gm respectively. It is seen that coercivity decreases with increase in doping but saturation magnetization increases with doping.
Nevertheless, saturation magnetization per impurity ion decreases with increase in doping concentration.

Figure 4.19: Magnetization curve of pristine and Mn doped CdO nanoparticles

The exact mechanism of intrinsic ferromagnetism in transition metal (TM) -doped oxides is still under debate. A diversity of theories has been proposed, such as super-exchange, double-exchange between the d states of TMs, free-carrier-mediated exchange and sp–d exchange mechanism, Rudermann- Kittel-Kasuya-Yosida (RKKY) etc. RKKY interaction is based on free electrons but CdO do not have free electrons like metals at such low doping. This is only suggestive; other possible mechanisms are also there that can explain the magnetic origin. Since any Cd\(^{+}\) centre related peaks are not seen in EPR spectra, so formation of bound magnetic polaron (BMP) by Cd\(^{+}\) ions with singly charged oxygen vacancy is not perfectly justified. So, here indirect interaction among Mn\(^{2+}\) (Mn-O-Mn) centres may lead to ferromagnetism, whereas direct interaction among them leads to antiferromagnetism. But with such diluted amount of Mn direct or indirect interaction is not possible. With increase in Mn doping, the average distance between Mn\(^{2+}\) ions decreases, resulting in enhancement of antiferromagnetic contribution [18-20]. It is well known that Mn ions belonging to antiferromagnetic clusters do not contribute to the increase in magnetic signal rather they reduce the net magnetization. Among all oxides of Mn, only MnO is anti-ferromagnetic with a Neel temperature of 96 K and Mn\(_3\)O\(_4\) is ferromagnetic with a curie temperature of 43 K. But Tc is very low, so entire
ferromagnetism cannot be due to Mn$_3$O$_4$. Also in our case, nano-clustering or MnO formation is ruled out as any impurity phase regarding Mn clustering was not observed in our XRD spectra. The formation of another type of BMP, in which an electron trapped in an oxygen vacancy (F center) couple with the magnetic spins of the nearest Mn$^{2+}$ ions within the radius of the hydrogen like orbit of the F center and forms a BMP, may lead to ferromagnetism. Electron locally trapped by oxygen vacancy, with the trapped electron occupying an orbital overlapping with the d shells of TM (Mn$^{2+}$) neighbors, has been proposed to explain the origin of ferromagnetism [21-24] in Mn doped CdO nanoparticles. The radius of the hydrogenic orbit of the F$^+$-center is given by $r_H = \varepsilon_r (m/m^*) a_0$ where $\varepsilon_r$ is the dielectric constant, m is the electron mass, $a_0$ is the Bohr radius. Those Mn$^{2+}$ ions that fall within this F-center radius interacts with the spin of F center, forms BMP and imparts ferromagnetism. These oxygen vacancies with single electron are called F$^+$ centre. PL spectra also confirm presence of two types of oxygen vacancies. Since electrons in doubly occupied oxygen vacancy (F centre) for $1S^2$ state generate only weak aniferromagnetic interaction, so BMP with singly charged oxygen vacancies are responsible for room temperature ferromagnetism (RTFM).

4.3 Conclusion

Following are the novel findings of our work in brief:

1. Cadmium interstitials which are Frenkel defects after getting higher energy go to the surface. At the surface after getting further higher energy these interstitial defects become oxidized and for this reason blue PL intensity which is due to Cd-interstitials first increases and then decreases.

2. Number of oxygen vacancies continuously increase with rise in temperature, so green PL intensity which is due to oxygen vacancies increases with rise in temperature.

3. Also, since F$^+$ centres are present in the samples so with rise in temperature, electrons trapped in oxygen vacancies get sufficient energy and become free
4.21 electrons. Hence conductivity and charge density increases with increase in temperature.

4. It was found that the incorporation of Mn in the host CdO nanoparticles leads to decrease in band gap. Also there is a partial quenching of luminescence intensity because of doping. Absence of any secondary oxide phases of Mn is confirmed. The origin of room temperature ferromagnetism can be assigned to formation of bound magnetic polaron.

References:


Chapter IV


