A Comparative Study of Optical and Magnetic Properties of Undoped and Cobalt Doped Manganese Oxide Nano Particles

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Abstract: Manganese oxide and Cobalt doped Manganese oxide nanoparticles are synthesized by solvothermal route using ethylene glycol as a solvent. The structural investigations are done by X-ray diffraction (XRD). The average grain size and lattice parameters are calculated. The particle size is confirmed by scanning electron microscope (SEM) analysis. The functional groups exists in the material are construed by Fourier transform infrared (FTIR) spectral analysis. The chemical composition and purity of the samples are inspected by using Energy-dispersive X-ray spectral analysis (EDAX). The optical properties are analyzed by Ultraviolet–Visible (UV-Vis) spectroscopy. A UV-Vis spectra shows that Cobalt doped Manganese oxide nanoparticles acquires blue shift. The magnetic properties of all the samples are reported using vibrating sample magnetometer (VSM) at room temperature. The values of saturation magnetization, retentivity, coercivity and squareness ratio are obtained from the magnetic studies.

Keywords: EDAX, FTIR, Solvo thermal method, UV-Vis, VSM and XRD

I. Introduction

Materials innovation and materials fabrication are at the heart of nanoscience and engineering. Nanoparticles are key focus of research for a wide novel application. At nanolevel the properties are greatly changed, as the size of the particles changed owing to the wide spread applications. Among nano materials magnetic nanoparticles are of extreme interest to researchers according to their very good magnetic properties. Magnetic nanoparticles have a wide range of applications, including magnetic fluids recording, catalysis, photo catalysis, electrochemical microwave absorption, magnetic resonance imaging, medical diagnosis, data storage and environmental remediation and as an electrode for supercapacitors and lithium ion batteries (LIB) [1]. The magnetic behavior of manganese oxide nanoparticles are of increasing research interest due to their large value of intrinsic magnetic moment [2]. Manganese oxides have attracted considerable interest as inexpensive and non-toxic alternative materials as rechargeable battery cathodes. The Cobalt doped Manganese oxide nano particles exhibited clear hysteresis showing typical ferromagnetic behavior, shows that the material formed is of soft magnetic material which is useful in magnetic memory devices. Various methods have been used to prepare nanoparticles. But, Microwave assisted solvothermal method is a chemical method that use microwave radiation for heating materials containing electrical charges for instance polar molecule in the solvent or charge ion in the solid. As compared to the other heating methods microwave assisted solution fabrication methods have got more focus of research because of rapid processing, high reaction rate, reduce reaction time and high yield of product [3]. In the present work, nanocrystalline particles of MnO₂ and Cobalt doped MnO₂ are prepared by solvothermal method. The synthesized nanoparticles are characterized by XRD, SEM, EDAX, FTIR, UV-VISIBLE and VSM.

II. Materials and Methods

2.1 Synthesis:

To prepare pure Manganese oxide nanoparticles, AR grade manganese acetate tetra hydrate [Mn (CH₃CO)₂ ∙ 4H₂O] and urea act as a catalyst was dissolved in ethylene glycol. The mixed solution was stirred well for 3 hour. The completely dissolved solution was kept in a domestic microwave oven. The microwave irradiation was carried out till the solvent evaporates completely. The prepared samples were washed four or five times with distilled water. Then the sample was washed with acetone to remove unwanted organic impurities present. The synthesized nanoparticles are filtered and dried in an oven at 323K. As a result of annealing to a high temperature 580K in a muffle furnace for 5h, the transition metal Manganese converted into their oxides to get pure Manganese Oxide nanoparticles.
To prepare Cobalt doped manganese oxide nanoparticles, analytical grade manganese acetate tetrahydrate \([\text{Mn}(\text{CH}_3\text{CO})_2\cdot4\text{H}_2\text{O}]\), Cobalt acetate dihydrate \([\text{Co}(\text{CH}_3\text{CO})_2\cdot2\text{H}_2\text{O}]\) and urea \([\text{CH}_4\text{N}_2\text{O}]\) are used as starting materials was dissolved in ethylene glycol (i.e.) \(\text{Mn}_x\text{Co}_{1-x}\text{O}(x=0.98, 0.96, 0.94 \text{ and } 0.92)\). The precipitates were washed four or five times with distilled water and acetone to eliminate other impurities. The synthesized nanoparticles are filtered and dried in an oven at 323K. On heating to a high temperature 580K in a muffle furnace for 5h to obtain Cobalt doped Manganese Oxide nanoparticles.

Compare the influence of dopant Cobalt 2%, 4%, 6% and 8% concentration on the structural, optical and magnetic properties with pure Manganese oxide nanoparticles.

2.2. Characterization Techniques:

The structural characteristics of formed \(\text{MnO}_2\) and cobalt doped \(\text{MnO}_2\) (2%, 4%, 6% and 8%) nanoparticles are determined by the aid of X-ray diffraction (XRD) (Bruker AXS D8 Advance model diffractometer using CuKα, \(\lambda=0.15406\text{nm}\) radiation). The morphology of the as-prepared sample is examined by Scanning electron microscope (SEM) (JEOL Model JSM - 6390LV). The functional groups and other impurities present in the material are interpreted by Fourier Transform Infrared spectroscopy (FTIR) (SHIMADZU MODEL –IR AFFINITY -1) in the wavelength range 400-4000cm\(^{-1}\). It is an added confirmation for the purity of the samples by using Energy-dispersive X-ray spectroscopy (EDAX). The optical properties are analyzed by Ultraviolet –Visible spectrometer (Model: Varian, Cary 5000) in the wavelength range 200-1000cm\(^{-1}\). Magnetic study is done by using vibrating sample magnetometer (VSM) (Model: LakeShore 7410).

III. Results and Discussion

3.1 X-Ray Diffraction Analysis:

The XRD patterns of pure and cobalt (2%, 4%, 6% and 8%) doped \(\text{MnO}_2\) nanoparticles are presented in Fig1. Diffraction patterns reveal that all the samples are of crystalline nature. All the diffraction peaks are well indexed to the orthorhombic structure \(\alpha = \beta = \gamma = 90^\circ\). The crystallite size was estimated using Debye Scherrer’s equation;

\[
D = \frac{k\lambda}{\beta\cos\theta} \text{(m)}
\]

Where, \(k \approx 0.9\), \(\lambda\) –Wavelength of the X-ray source (1.5406 Å), and \(\beta\) – Full width half maximum (FWHM) of a diffraction peak.

The lattice constants \(a, b, c\) and the volumes are evaluated from XRDA software and the estimated values are recorded in Table 1.

![Fig.1 – XRD spectrum of (a) Pure Manganese Oxide (b) Cobalt doped Manganese Oxide nanoparticles](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size</th>
<th>Lattice parameter (Å)</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Manganese Oxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cobalt doped Manganese Oxide</td>
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</table>

Table1: The Variation Of Particle Size And Lattice Parameters Of \(\text{MnO}_2\): Co Nanoparticles
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<p>| | | | | |</p>
<table>
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<tr>
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</thead>
<tbody>
<tr>
<td>MnO₂</td>
<td>39.4</td>
<td>9.2772</td>
<td>4.4900</td>
<td>2.8221</td>
</tr>
<tr>
<td>MnO₂: Co (2%)</td>
<td>36.2</td>
<td>9.2558</td>
<td>4.4870</td>
<td>2.8229</td>
</tr>
<tr>
<td>MnO₂: Co (4%)</td>
<td>34.7</td>
<td>9.1703</td>
<td>4.5673</td>
<td>2.7747</td>
</tr>
<tr>
<td>MnO₂: Co (6%)</td>
<td>32.8</td>
<td>9.3049</td>
<td>4.5035</td>
<td>2.8188</td>
</tr>
<tr>
<td>MnO₂: Co (8%)</td>
<td>32.1</td>
<td>9.1747</td>
<td>4.4733</td>
<td>2.8614</td>
</tr>
</tbody>
</table>

3.2 Scanning Electron microscope analysis:
The SEM is widely used to identify phases based on qualitative chemical analysis and crystalline structure. Backscattered electron images can be used for rapid discrimination of phases in multiphase samples. The SEM analysis was carried out to investigate the detailed morphology of the synthesized pure MnO₂ and cobalt doped MnO₂ nanoparticles with different dopant concentrations (2%, 4%, 6% and 8%) are shown in Fig 2.

3.3 Fourier transform infrared spectral analysis:
FTIR spectrum was used to identify functional groups and other impurities present in the MnO₂ and Cobalt doped MnO₂ nano system with dopant concentration (2%, 4%, 6% and 8%) is presented in Fig3. FTIR spectra of undoped and different levels of Cobalt incorporated MnO₂ nano crystals are recorded in the range 4000 – 400 cm⁻¹.
3.4 Energy-dispersive X-ray spectral analysis (EDAX):

Quantitative analysis of Cobalt (2%, 4%, 6% & 8%) doped MnO$_2$ is put down in the pie chart. It is seen that no impurities are found out. Energy dispersive X-ray spectroscopy (EDAX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum. The emission of characteristics X-rays from a specimen, a high energy beam of charged particles such as electron or protons or a beam of X-rays, is focused into the sample being studied.
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Fig. 4 – EDAX spectrum of (a) 2% Cobalt doped Manganese Oxide, (b) 4% Cobalt doped Manganese Oxide, (c) 6% Cobalt doped Manganese Oxide & (d) 8% Cobalt doped Manganese Oxide

3.5 UV-Visible Spectral Analysis:
UV-Visible spectra illustrate that pure Manganese Oxide nanoparticles exhibits maximum absorbance at 376 nm. Fig. 5 (a) shows the Ultraviolet – Visible absorbance spectra of pure MnO$_2$ nanoparticles. Direct band gap of MnO$_2$ is determined by fitting the absorption data to the transition equation $\alpha h\nu = A (h\nu-E_g)^2$. Optical band gap energy $E_g$ = 3.15 eV was obtained by extrapolating the linear part of the curve $(\alpha h\nu)^2$ versus photon Energy $h\nu$ (eV) known as Tauc plot in Fig. 5(b).
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The Cobalt doped Manganese oxide nanoparticles acquire blue shift from the pure MnO$_2$ nanoparticles and absorption wavelengths of dopant concentration 2%, 4%, 6% and 8% are 280nm, 273nm, 270nm and 265nm from UV-Vis absorption spectra in Fig.6-(a).

![Fig.6](image)

**Fig.6-** UV-Visible absorption spectrum of Cobalt doped MnO$_2$ Nano particles

From the Tauc plot band gap energy of Cobalt doped Manganese Oxide nanoparticles are measured 4.43eV, 4.545eV, 4.496eV and 4.682eV as shown in Fig.-7 (a), (b), (c) & (d).

![Fig.7](image)

**Fig.7-** Tauc plot of (a) 2% Cobalt doped Manganese Oxide, (b) 4% Cobalt doped Manganese Oxide, (c) 6% Cobalt doped Manganese Oxide & (d) 8% Cobalt doped Manganese Oxide
3.6 Magnetic Properties:

As prepared MnO₂ nanoparticles are intermediate product [4]. The magnetic properties of synthesized MnO₂ nanoparticles are characterized by VSM and obtained the hysteresis loops are shown in Fig 8. The M-H curve is linear with low coercivity (10.767 gauss). Due to the amount of increasing the dopant concentration, the size of the particle decreases with greater coercivity. The nanosystem gain their single domain character with their spins are aligned parallel. The magnetic parameters are recorded in Table 2.

![Magnetic Properties:](image)

**Fig.8-** Magnetic Hysterisis loop of (a) Undoped Manganese Oxide (b) 2% Cobalt doped Manganese Oxide, (c) 4% Cobalt doped Manganese Oxide (d) 6% Cobalt doped Manganese Oxide; (e) 8% Cobalt doped Manganese Oxide

**Table 2:** Magnetic Parameters From Hysteresis Loop

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>COERCIVITY (gauss)</th>
<th>MAGNETIZATION (memu)</th>
<th>RETENTIVITY (µemu)</th>
<th>SQUARENESS RATIO (SQR) (M_r/M_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂</td>
<td>10.767</td>
<td>23.489</td>
<td>17.485</td>
<td>0.7443</td>
</tr>
<tr>
<td>MnO₂:Co(0.02)</td>
<td>393.61</td>
<td>23.786</td>
<td>956.23</td>
<td>0.0402</td>
</tr>
<tr>
<td>MnO₂:Co(0.04)</td>
<td>398.71</td>
<td>35.712</td>
<td>108.16</td>
<td>0.0302</td>
</tr>
<tr>
<td>MnO₂:Co(0.06)</td>
<td>401.75</td>
<td>30.703</td>
<td>878.03</td>
<td>0.0285</td>
</tr>
<tr>
<td>MnO₂:Co(0.08)</td>
<td>408.33</td>
<td>29.890</td>
<td>861.38</td>
<td>0.0288</td>
</tr>
</tbody>
</table>

IV. Discussion

The particle size reduces with increase of dopant concentration. The Bragg reflections from (200), (110), (210), (310), (011), (400), (211) and (320) planes which corresponds to MnO₂ (JCPDS 82-2169). The value of crystallite size of pure manganese oxide is equal to 39nm [5]. Due to the smaller shift in angle of diffraction, the lattice parameters also slightly varied (±10%).

The SEM image shows that having spherical geometry. It consists of irregular particles with a variety of pores due to the evolution of large amount of gases that are formed as by product during synthesis [6]. The size of the nanoparticles 30nm to 40nm is very agreed with the SEM analysis by Image J software.
A close interpretation of the FTIR spectra reveals metal oxides generally give absorption bands below 1000 cm\(^{-1}\) that arise from interatomic vibrations of nanoparticles. It represents the band at 533.35 cm\(^{-1}\) and 666.73 cm\(^{-1}\). This executed vibration bands could be assigned as metal – oxygen (Mn-O) bending vibrations [7]. The vibration band at 478.35 cm\(^{-1}\) and 486.06 cm\(^{-1}\) shows the existence of Co-O stretching vibration mode. The intensity of Co-O stretching bond increases with increasing the concentration of Cobalt [8]. The wavenumber 1392.22 cm\(^{-1}\) and 1342.46 cm\(^{-1}\) represents O\(_2\) stretching frequency [9]. A stretching frequency at 3394.72 cm\(^{-1}\) and a weak asymmetric band at 1566.20 cm\(^{-1}\) support the presence of hydroxyl (–OH) group due to the absorption of water by nanoparticle during the sample preparation[10]. The wavenumber 2299.15 cm\(^{-1}\) and 2376.30 cm\(^{-1}\) assigned to the CO\(_2\)mode. The CO\(_2\) modes are present in the FTIR spectra not owing to the serious contamination in Co doped MnO\(_2\) but these modes due to atmospheric CO\(_2\) in the samples. Samples might have trapped some CO\(_2\) from the atmosphere during FTIR characterization might have given such modes [11&12].

EDAX allows the elemental composition of the specimen to be measured. The energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. EDAX spectrum shows the presence of dominant elements Manganese, Oxygen, and Cobalt.

MnO\(_2\) nanoparticles have very high absorbance in the visible region. Cobalt doped MnO\(_2\) nanoparticles absorption peaks shift towards smaller wavelength (higher band gap energy) as their crystal size decreases. So the prepared samples are used in solar cells and photo-catalysts [13].

The addition of ferromagnetic material like Cobalt with anti-ferromagnetic material MnO\(_2\) results in ferromagnetic nature. The field necessary to reduce the net moment to zero is defined as the coercive field (\(\mu_0H_c\)) or anisotropy field. The coercivity increases with dopant concentration increases but retentivity is decreases. The Cobalt doped Manganese oxide nano particles exhibited clear hysteresis showing typical ferromagnetic behavior that is ‘positive spin interactions’ when the spins are aligned in one single direction, having non-zero coercivity and retentivity. The area of the hysteresis curve is very small. This shows that the material formed is of soft magnetic material which is useful in magnetic memory devices [14]. In general large SQR values are desired for recording medium. Hc is a very complicated parameter for magnetic films and is related to the reversal mechanism and the magnetic microstructure, i.e., shape and dimensions of the crystallites, nature of the boundaries, and also the surface and initial layer properties, etc.

V. Conclusion

MnO\(_2\) and Cobalt doped MnO\(_2\) Nanoparticles were successfully synthesized by the solvothermal method employing microwave irradiation. XRD, SEM FTIR, EDAX UV-Vis and VSM studies are carried out. The XRD spectrum shows the samples are in single phase. The pure and Cobalt doped nanoparticles are having orthorhombic structure. The particle sizes of synthesized pure MnO\(_2\) nanoparticles are 38nm. For Co doped MnO\(_2\) samples the particle size decreases. The FTIR spectra and EDAX spectra indicate the formation of Pure and Co doped MnO\(_2\) nanoparticles. UV-Vis spectra illustrates that Cobalt doped Manganese oxide nanoparticles acquire blue shift from the bulk MnO\(_2\) nanoparticles (i.e.) 3.15 eV. Energy band gap increases with Cobalt concentration due to the effect of quantum confinement. The magnetic studies reveal the room temperature ferromagnetic behaviour of Cobalt doped MnO\(_2\) nanoparticles. The prepared Samples can be used as soft electro-magnetic materials. Then, focus on electrical studies for further analysis, the most promising electrode material Manganese oxide in lithium-ion batteries and super capacitor applications with the effect of dopant concentration.

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