CHAPTER V: COVERS MICROWAVE SYNTHESIS AND PREPARATION OF COBALT OXIDE NANOSTRUCTURES WITH VARIABLE PARAMETERS SUCH AS CALCINATION TEMPERATURES, SURFACANTANTS, MICROWAVE POWERS AND VARIOUS METAL DOPANT EFFECTS FOR THE IMPROVEMENT OF MAGNETIC PROPERTIES.
5.1 INTRODUCTION

The development of recent information technologies resulted in fundamental changes of our society, and this development has never been achieved without magnetic materials. At first, it is believed that atomic magnetic moments are assumed parallel and all the materials are ferromagnetic in nature. But, Louis Neel (1949) predicted that very small particles might belong to super paramagnetic nature at finite temperature and also the direction of magnetization fluctuated within the materials owing to the impact of thermal agitation. It is important to note that many recent applications such as data storage, spintronics, biomedicine and telecommunications are mainly based on the use of nanostructured materials with magnetic properties that often differ considerably from those of bulk materials [1]. Among nanostructured magnetic materials, the spinel cobalt oxide (Co$_3$O$_4$) is an important magnetic material targeted on enormous potential applications such as heterogeneous catalysts, anode materials in Li ion rechargeable batteries, solid-state sensors, electro chromic devices, solar energy absorbers, pigments, and so on [2]. The development of Co$_3$O$_4$ towards the applications in numerous fields, the material is synthesized in nano level with well controlled physical and chemical properties.

The particle size and morphology of Co$_3$O$_4$ influences the most important changes in the physical properties of nanomaterials. The controlled preparation of Co$_3$O$_4$ particles with completely different sizes and morphologies is a challenging research area. Many reports are available for the preparation of Co$_3$O$_4$ with various structures including nanobelts [3], nanorods [4], nanospheres [5], nanocubes [6], nanowires [7] and nanoflowers [8] etc. For example, Co$_3$O$_4$ nanospheres are successfully synthesized by Farhadi et al and they showed weak
ferromagnetic behavior with narrow size distribution and Park et al have also reported nanosphere like morphologies with excellent performance of toluene and acetone gas sensing vapors [9-10]. Hao et al have showed sheet like morphology of Co$_3$O$_4$ for better electrochemical performance with excellent capacitance stability [11]. Co$_3$O$_4$ nanocubes are reported by Sun et al and the nanocube like Co$_3$O$_4$ showed higher gas sensing performance of xylene and ethanol at low operating temperatures [12].

The interest for the preparation and application of nanometer size materials is increasing since they exhibit better properties for industrial applications. Different methods are attempted to synthesize nanostructured Co$_3$O$_4$ materials such as sol-gel, precipitation, laser ablation, sonochemical and thermal decomposition [13-17]. All these methods were greatly used to control over the nanorange preparation, but still these preparation methods were not giving uniform sized particles. Recently, microwave reaction method was largely adopted for the preparation of well structured nanosized materials with increased physical properties. Microwave energy assisted heating with electromagnetic frequencies ranging from 0.3 to 300 GHz has been widely used for the preparation of nanomaterials because of its efficient fast heating and cooling rates, which cannot be achieved in any conventional heating process [18].

Different unique Co$_3$O$_4$ nanostructures have been synthesized using microwave energy. The porous Co$_3$O$_4$ nanosheet is synthesized by microwave reaction that shows larger capacitance values of 1235 mAh$^{-1}$ with increased electrical conductivity and mechanical stability [19]. The well dimensionality of Co$_3$O$_4$
nanowires is synthesized from microwave which exhibits low temperature ferromagnetism and superior applications in super capacitor with improved cycle stability and higher capacity [20]. The observation of weak ferromagnetic nature for Co$_3$O$_4$ nanoparticles at room temperature is examined by Bhatt et al with the effect of finite size and uncompensated surface spins [21]. According to Ai et al, the existence of small hysteresis loop for spinal Co$_3$O$_4$ nanostructures and their magnetization value linearly increases with the applied field [22]. From these reports, microwave energy is employed to provide nanostructured Co$_3$O$_4$ with increased properties, finds considerable applications in numerous industries and fields.

In this chapter, our aim is to elucidate the size and shape dependence of Co$_3$O$_4$ crystallites on magnetic properties by the following different manner.

a) Effect of surfactants, calcination temperatures on Co$_3$O$_4$ nanoparticles

b) Preparation of nanoparticles using microwave and hydrothermal methods and comparative studies

c) Transition and rare earth metal doped Co$_3$O$_4$ nanoparticles

The prepared samples are analyzed to find their structural, optical, morphological and magnetic properties using XRD, FTIR, Raman, PL, SEM, XPS, and VSM.

5.2 EXPERIMENT

5.2.1 Materials Synthesis

a) Synthesis and calcination of Co$_3$O$_4$ NP’s with different calcination temperatures

In a typical synthesis of Co$_3$O$_4$ nanoparticles, required amount of cobalt acetate was dissolved in 50 ml distilled water and stirred for 5 min at room temperature. Simultaneously, 3 ml ammonia was added drop wise into this aqueous solution
under vigorous stirring with the control of pH around 9. In addition to that, 0.5 g of citric acid was added as a capping agent. Then, the solution was transferred to poly propylene capped autoclave bottles. The container is ready for microwave treatment in a microwave oven (Samsung CE1031LFB) which works with a frequency of 2.45 GHz having a maximum microwave power of 900 W. The synthesized solution was treated by microwave radiation with the power of 180 W for 15 minutes. The system was then allowed to cool to room temperature. The resultant products deposited at the bottom of the vessel were collected by centrifugation and the precipitates were rinsed with distilled water to remove soluble ions and subsequently left to dry at 80 °C in hot air oven for 12 hrs and calcined at different temperatures. The obtained cobalt oxide (Co$_3$O$_4$) nanoparticles were named as C4, C5, C6, C7 and C8 for the corresponding 400 °C, 500 °C, 600 °C, 700 °C and 800 °C calcination temperatures.

b) Synthesis procedure for surfactant added Co$_3$O$_4$ samples

In a typical experiment, three batches of solutions were prepared by dissolving 2g of Co(NO$_3$)$_2$.6H$_2$O in 50 ml distilled water and vigorously stirred by magnetic stirrer to form a transparent solution. A required amount of surfactant (CTAB, Citric and Hexamine) was taken in each separate cobalt solutions. Then 3 ml of ammonia solution was added drop wise to form a clear solution at pH 9. The resulting solution was then transferred to poly propylene capped autoclave bottles of 100 ml capacity. The solutions were subjected to microwave radiation with the power of 300 W for 5 min duration. After the complete reaction process, the autoclave bottles were cooled to room temperature, then the brown precipitates of Co$_3$O$_4$ was separated by centrifugation and the precipitates were rinsed with distilled
water and ethanol for several times to remove soluble ions. The precipitate was
dried at 80 °C in a hot air oven for 12 h and then the as-prepared powder was
calcined under air at 500 °C for 2h to obtain oxide nanostructures from hydroxide
structures.

c) **Synthesis procedure for RE and TM doped Co₃O₄ samples**

For the synthesis of cerium doped Co₃O₄, required amounts of Co(NO₃)₂·6H₂O
and Ce(NO₃)₂·6H₂O with different mol ratios (Co:Ce : 1.98:0.02, 1.94:0.06,
1.90:0.10 and 1.80:0.20) were dissolved in 50 ml distilled water separately and
vigorously stirred by magnetic stirrer to form a transparent solution. Next, 3 ml of
ammonia solution was added drop wise to form a clear solution at pH 9. The
resulting solution was transferred to poly propylene capped autoclave bottles of
100 ml capacity and then subjected to microwave radiation with the power of
300 W for 5 min duration. After completing the reaction process, the same
procedure as mentioned earlier was adopted for the preparation of Ce-Co₃O₄
samples. Same procedure was adopted for TM (Ni, Mg, Zn and Fe) doped Co₃O₄
samples by adding 3% TM(NO₃)₂·6H₂O instead of Ce(NO₃)₂·6H₂O and repeated
all the above steps to prepare TM (Ni, Mg, Zn and Fe) doped Co₃O₄ samples.

5.2.2 **Characterization Techniques**

The synthesized Co₃O₄ samples were subjected under X-ray powder diffraction
(XRD) using PANalytical model XPERT-PRO X-ray diffractometer for
identifying the phase and crystalline nature. The thermal behaviours of the
synthesized materials were characterized from Perkin-Elmer Thermal Analysis
system with a heating rate of 20 °C/min. Thermo Nicolet 380 FT-IR spectrometer
with the range of 400–4000 cm⁻¹ was used to analyze the presence of functional
groups of synthesized precursor. The morphologies of the products were examined using a scanning electron microscopy (SEM) (JSM-6390). Room temperature photoluminescence spectra of the Co$_3$O$_4$ nanoparticles were recorded using Cary Eclipse PL spectrograph. The Raman spectra were taken from the imaging spectrograph STR 500 mm focal length laser Raman spectrometer (SEKI Japan). X-ray photoelectron spectrometry (XPS) analysis was applied to find the presence of metal-oxygen. Vibrating sample magnetometer (Lakeshore VSM 740) was used to determine the room and low temperature magnetic properties of the materials.

5.3 RESULTS AND DISCUSSION

5.3.1 Thermal Characterization

The thermogram (TGDTA) of as synthesized sample is shown in Fig. 5.1(a). It is observed that the weight loss occurs in two major steps. In the first step, temperature up to 200 °C shows 15.28% weight loss owing to the elimination of water content from as synthesized sample. From the range of 200 - 455 °C, 29% weight loss is observed because of the removal of carbonate and acetate related species from the sample. The formation of Co$_3$O$_4$ nanoparticles started around 455 °C and at this temperature a sudden decrease of mass change is observed. There is no further weight loss occurred above 455 °C as shown in Fig 5.1(a). It is predicted that, if the sample calcined above 455 °C will leads to complete decomposition of hydroxide, acetate related species and transform into Co$_3$O$_4$ nanoparticles [23]. From this TG/DTA results, it has been decided to subject the synthesized sample above 500 °C as calcination temperature.

Fig. 5.1(b) displays the TGA curve of 10% Ce mixed β-Co(OH)$_2$ sample. A two-step weight loss has been observed from the TGA curve. The weight loss occurs below 140 °C is an indication of removal of water related content in
Co(OH)$_2$ sample. The weight loss occurring from 140 to 290 °C is due to the decomposition process of metal hydroxides as well as desorption of nitrate residuals. It is concluded from the TGA curve that the formation of Co$_3$O$_4$ is started around 350 °C, and there is no further weight loss at higher temperature which indicates the absence of additional phase or any other structural changes in the sample [24-26].

Fig. 5.1: Thermogram of a) undoped Co$_3$O$_4$ sample and b) 10% Ce mixed Co$_3$O$_4$ cubic structures
5.3.2 Structural Characterization

The phase and crystalline nature of Co$_3$O$_4$ nanoparticles were investigated for calcined samples synthesized under different temperatures of 400°C, 500°C, 600 °C, 700°C and 800 °C by X-ray diffraction method. The cubic phase nature with optimum size and well matched lattice parameters with standard JCPDS of 26-4356 was obtained for 600 °C calcined sample and this temperature is also well supported by thermal analysis. To understand more, we have decided to synthesize Co$_3$O$_4$ nanoparticles with the calcination range between 400 °C to 800 °C based on the results of our different calcined work.

In all our work, we obtained cubic phase nature of Co$_3$O$_4$ nanoparticles with 2θ values 31.3°, 36.9°, 44.9°, 59.4°, and 65.3° which are well matched with the standard JCPDS of 26-4356 (Fm3m, 4.261 Å) [27]. The formation of cubic phase of Co$_3$O$_4$ using different surfactants, different methods, and variation of microwave powers and dopants used Co$_3$O$_4$ samples is confirmed by using XRD pattern shown in Fig. 5.2 (a-e). For the case of TM and RE doped Co$_3$O$_4$ samples, no peaks related to dopant ions and other impurities of dopant oxides such as CeO$_2$, Ce$_2$O$_3$ or other crystalline forms were detected from all the patterns (Fig. 5.2 (d & e)) which confirm that dopant ions were uniformly substituted in Co lattice sites. And hence it is confirmed that the introduction of TM and RE ions does not change the crystal structure of Co$_3$O$_4$.

The crystallite size and strain of Co$_3$O$_4$ nanoparticles were estimated using Williamson-Hall method

\[ \beta_{\text{total}} = \beta_{\text{size}} + \beta_{\text{strain}} = \left( \frac{K\lambda}{D_{\text{XRD}} \cos \theta} \right) + 4\eta \tan \theta \]

where \( \lambda \) is the X-ray wavelength, \( \beta \) is the FWHM (full width at half maximum intensity), \( \theta \) is the Bragg’s angle and \( \eta \) is the micro strain parameter [28].
Fig. 5.2: XRD patterns of Co$_3$O$_4$ using different a) Surfactants, b) Methods c) Microwave powers, d) Metal doped (M=Ni, Mg, Zn & Fe) and e) Ce doped Co$_3$O$_4$ cubic structures.
Fig. 5.3: Williamson-Hall plot for Co$_3$O$_4$ cubic structures for different calcined samples

(a-c), d) 10% Ce mixed Co$_3$O$_4$ and e) CTAB assisted Co$_3$O$_4$. 

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The crystallite sizes obtained from W-H plot of PXRD is in good agreement with the ones measured with the Debye-Scherrer’s formula. Fig. 5.3 (a-e) gives the plot for \( \beta_{\text{total}} \cos \theta / K \lambda \) versus \( 4 \sin \theta / K \lambda \) for the samples prepared by using different calcined, Ce doped and CTAB added samples. The linear fit using W-H plot provides different strain values by different slope values and the line interception with y-axis gives the inverse crystallite size. From this W-H correlation, the crystallite sizes were found to be nanosize for all the samples.

Moreover, the crystallite sizes were found to be very less for 600 °C calcined and Ce incorporated Co₃O₄ than other samples. The observations of crystallite size and strain from the W–H plot for all the samples are presented in Table 5.1 and 5.2. The reduced crystallite size of less than 25 nm was observed for CTAB and citric acid added Co₃O₄ samples than hexamine added sample and their corresponding strain and dislocation density values are also provided in Table 5.1.

The preparation of Co₃O₄ sample by microwave method produced less crystallite size (20 nm) and hence microwave method is more suitable to prepare nanocrystalline Co₃O₄ materials than any other methods. In microwave method, different microwave powers are used and the samples prepared with lower powers exhibit crystallite size less than 30 nm while using higher microwave power leads to the formation of aggregation of particles which resulted increased crystallite sizes. In similar way, the reduced crystallite size was observed for transition metal and rare earth (Ce) doped Co₃O₄ samples.
### Table 5.1: Crystallite size and strain values for Co₃O₄ samples prepared by using different surfactants, different methods and various microwave powers

<table>
<thead>
<tr>
<th>Lattice Parameters</th>
<th>Surfactants</th>
<th>Methods</th>
<th>Microwave</th>
<th>Hydrothermal</th>
<th>900 W</th>
<th>600 W</th>
<th>450 W</th>
<th>300 W</th>
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<tr>
<td></td>
<td>CTAB</td>
<td>CA</td>
<td>H</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>Average Crystallite size from XRD (nm)</td>
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<td>20.9</td>
<td>41.8</td>
<td>20.9</td>
<td>30.8</td>
<td>31.1</td>
<td>26.9</td>
<td>25.4</td>
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<tr>
<td>Micro Strain $10^3$ (Lines/m)</td>
<td>1.4</td>
<td>1.6</td>
<td>0.8</td>
<td>1.6</td>
<td>1.1</td>
<td>1.1</td>
<td>1.28</td>
<td>1.3</td>
</tr>
<tr>
<td>Dislocation Density $15^2$ (Lines/m)</td>
<td>1.8</td>
<td>2.28</td>
<td>0.58</td>
<td>2.2</td>
<td>1.0</td>
<td>1.03</td>
<td>1.3</td>
<td>1.5</td>
</tr>
</tbody>
</table>

### Table 5.2: Crystallite size and strain values for Co₃O₄ samples prepared by using different TM dopants, RE ion dopant and different calcined samples

<table>
<thead>
<tr>
<th>Lattice Parameters</th>
<th>TM dopants</th>
<th>RE dopant</th>
<th>Calcination</th>
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<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Fe</td>
<td>Mg</td>
</tr>
<tr>
<td>Average Crystallite size from XRD (nm)</td>
<td>16.7</td>
<td>8.3</td>
<td>20.9</td>
</tr>
<tr>
<td>Micro Strain $10^3$ (Lines/m)</td>
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<tr>
<td>Dislocation Density $15^2$ (Lines/m)</td>
<td>3.5</td>
<td>14.2</td>
<td>2.2</td>
</tr>
</tbody>
</table>
5.3.3 Functional Analysis

The FTIR spectra of Co$_3$O$_4$ samples using different conditions are shown in Fig. 5.4(a-f). First, the functional property of as synthesized Co$_3$O$_4$ sample is analyzed and it shows the peak appeared at 3381 cm$^{-1}$ owes to the presence of water within the sample (Fig. 5.4(f)). The peak found at 1405 cm$^{-1}$ is assigned to the stretching vibration of $\nu$ (OCO$_2$). The set of peaks exhibited between 1580-1250 cm$^{-1}$ is due to the nature of carbonate species in the synthesized sample. The peaks exhibited below 600 cm$^{-1}$ are due to the vibration of metal oxygen and Co-OH of the products [29-30]. It is carefully evaluated from the previous literature reports that the peaks appeared around 577 and 663 cm$^{-1}$ in FTIR spectra are due to spinel structure of Co$_3$O$_4$, the former peak can be assigned to the stretching vibration mode of M–O in which M is Co 3$p$ and the later band is attributed to Co 2$p$ ions [31].

The missing of Co–O stretching band around 550–580 cm$^{-1}$ when calcination temperature was above 600 °C may be due to the reduction of oxygen which turns the deformation of spinel structure into Co 2$p$ ions. It is confirmed that, the calcinates temperature above 600 °C is not suitable to retain its spinal structure. The absence of the other peaks in these spectra confirmed the purity of Co$_3$O$_4$ nanoparticles and therefore the samples are free from impurities [32-34]. In these spectra, the peak related to OH stretching is not observed for calcined samples.

The FTIR spectra of the samples prepared with different surfactants, microwave powers, transition metal, rare earth metal and different methods have shown two strong peaks which are due to the presence of metal oxygen in the samples. The small wave number change is noticed and it is mainly due to the function of varying the parameters to synthesize Co$_3$O$_4$ nanoparticles.
Fig. 5.4: FTIR spectra of Co$_3$O$_4$ using different a) Surfactants, b) Methods c) Microwave powers, d) Metal doped (M= Ni, Mg, Zn & Fe), e) Ce doped and e) Different calcinated samples.
5.3.4 Morphological Characterization

a) Calcination Temperatures Effect

The SEM images of Co$_3$O$_4$ nanoparticles calcined at 400 °C, 600 °C and 800 °C are displayed in Fig. 5.5(a-c). Fig. 5.5(a) represents morphological images of Co$_3$O$_4$ nanoparticles calcined at 400 °C that showed microsphere like structures with high degree of agglomeration. Fig. 5.5(b) shows, uniform sized spherical shaped nanoparticles obtained for Co$_3$O$_4$ calcined at 600°C. The size of spherical shaped nanoparticles is smaller than the sample calcined at 400 °C and 800 °C. This may be related to the appropriate selection of calcination temperature which is used to produce finite size and shaped particles. The larger size non uniform particles were obtained for the sample calcined at 800 °C as a result of the aggregation of uniform sized particles into highly agglomerated particles.

In chemical synthesis process, it is noted that the particles are agglomerate for higher calcinations temperature and exhibit particles with larger dimension. By increasing the calcinations temperature from certain limit and duration time, the synthesized particles aggregate and become larger by agglomeration. Many groups have reported such agglomeration [35-37]. This result can also be confirmed from our XRD patterns where the identified peaks and become narrow by increasing the calcinations temperature.
**Fig. 5.5:** SEM images of Co$_3$O$_4$ using a-c) different calcinations of 400 °C, 600 °C and 800 °C, and d) CTAB, e) Citric acid

**Fig. 5.6:** a) SEM images of undoped Co$_3$O$_4$ and (b-e) Metal doped (M=Ni, Mg, Zn & Fe) Co$_3$O$_4$ cubic structures
Fig. 5.7: SEM images of Co$_3$O$_4$ with different Ce contents: (a) 0%, (b) 1%, (c) 3%, (d) 5%, and (e) 10%

Fig. 5.8: a) EDX images of undoped Co$_3$O$_4$ and (b-f) Metal doped (M=Ni, Mg, Zn, Fe & Ce) Co$_3$O$_4$ cubic structures
b) Surfactant Effect

The CTAB added Co$_3$O$_4$ sample is having hexagonal stacked plate like structure as shown in Fig. 5.5(d). The specific morphology is mainly attributed from the addition of CTAB which serves as intermediate complex and the presence of CTAB causes the formation of plate and flake like structures with reduced dimensions. Fig. 5.5(e) represents spherical nature of morphology due to the addition of weak acid i.e. citric acid which prevents the faster growing faces in Co$_3$O$_4$ nanostructures.

c) TM dopant effect

The effect of metal dopants in Co$_3$O$_4$ lattice has been investigated by scanning electron microscope and their morphological nature is presented in Fig. 5.6(a-e). Fig. 5.6(a) shows hexagonal plate morphology with higher degree of agglomeration for pure Co$_3$O$_4$. The addition of dopants has improved hexagonal plates structures than pure Co$_3$O$_4$. Using these dopants, one can improve the morphology with suitable concentration of metal dopants. When concentration of dopant level increases from certain limit, the particles aggregates and the morphology will be dissolved.

d) RE dopant Effect

The morphological nature of pure and cerium doped Co$_3$O$_4$ sample is displayed in Fig. 5.7(a-e). The plate like morphology was observed for 1% cerium incorporated Co$_3$O$_4$ sample and this plate like structure is changed into highly agglomerated irregular structure for increased concentration of cerium in Co$_3$O$_4$ as shown in Fig. 5.7(c-e). From these SEM images, it is evidenced that doping of low level cerium promotes improved morphology of Co$_3$O$_4$ nanostructures with reduced
agglomeration and higher uniformity. The elemental analysis (EDX) spectra for 3% metal (Ni, Mg, Zn and Fe) and 10% Ce doped Co$_3$O$_4$ are compared with pure Co$_3$O$_4$ and their corresponding images illustrated in Fig. 5.8(a-f). These spectra indicate the presence of metals such as Co, Ce, and O atoms as the major chemical components in the samples. The experimentally obtained compositions of Co, Ce and O elements were consistent with the theoretically calculated values which confirms the presence of cerium in Co$_3$O$_4$ lattice site synthesized by microwave method. Similar comparisons were made for metals doped Co$_3$O$_4$ samples.

5.3.5 Optical Properties

The photoluminescence property of calcined Co$_3$O$_4$ nanoparticles is investigated at room temperature and the corresponding spectra for the samples using CTAB, citric acid, different calcination temperatures (C4, C6 and C8) and Ce doped Co$_3$O$_4$ are shown in Fig. 5.9(a-d). It is well known that the optical properties of Co$_3$O$_4$ nanoparticles are closely dependent on their structures and morphologies. In metal oxide nanostructures, the PL emission is usually classified into two sections including near band edge (NBE) UV emission and deep level (DL) defect associated visible emission.

The UV emission is commonly attributed to the direct recombination of the excitons through an exciton–exciton scattering. The visible emission originates from the radiative recombination of a photo-generated hole caused by the impurities and structural defects in the sample, for instance, oxygen vacancies and cobalt interstitials. In general, the emission spectrum of Co$_3$O$_4$ sample is having two emission bands at 200–380 and 400–580 nm wavelength ranges.

The first band can be assigned to $O^{2-} \rightarrow Co^{2+}$ charge-transfer process whereas the second one related to $O^{2-} \rightarrow Co^{3+}$ charge transfer [38-41]. The broad
peak exhibited at 372 nm for all the samples is undoubtedly due to near band edge UV emission. In addition to that, a shoulder peak found at 365 nm is due to the impact of calcination temperatures and this peak is slightly shifted with reference to each sample shown in Fig. 5.9(c). The set of peaks observed at 492 nm and 520 nm are belonged to green emission. It is noted from the entire spectrum that, the intensity of UV emission is dominated over visible emission revealed that the surface morphology plays an important role for the determination of optical properties. It is evinced from the previous reports that, irradiative transitions between shallow donors (related to oxygen vacancies) produces strong UV emission and suppressed visible emission confirmed the good crystalline nature of the Co$_3$O$_4$ nanoparticles [42].

The characteristic emission bands centered at 360, 492 and 520 nm are equivalent to the band gap of 3.44 eV, 2.52 eV and 2.38 eV, respectively for pure and doped Co$_3$O$_4$ samples. The optical transition attributed to violet emission at 3.44 eV is due to the band gap transition of O$^{2-}$ $\rightarrow$ Co$^{2+}$ charge transfer process and the transition occurred at 2.52 and 2.38 eV is ascribed to green emission due to the charge transfer process of O$^{2-}$ $\rightarrow$ Co$^{3+}$ [43]. For undoped Co$_3$O$_4$, no peaks were observed other than these three emissions and when Ce is introduced into the lattice, another emission is observed at 462 nm and the emission peaks intensities increased with the increase of Ce content. The optical transition at 3.44 eV is attributed to a band gap transition from the valence band of the Co$_3$O$_4$, which comprises a mixture of Co$^{2+}$, 3$d$ and O 2$p$ states. The lower energy transitions at 2.68, 2.52 and 2.38 eV are assigned to transitions from mid gap states into the conduction band due to the presence of cerium within Co$_3$O$_4$. 

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Fig. 5.9: Photoluminescence spectra of Co$_3$O$_4$ using a) CTAB, b) Citric acid c) Different calcinations and e) Ce doped Co$_3$O$_4$ cubic structures
5.3.6 Raman and XPS analyses

Fig. 5.10 shows the Raman spectra of undoped and Ce doped Co$_3$O$_4$ samples. For pure and doped Co$_3$O$_4$, five Raman peaks were found at 185, 460, 506, 593, and 658 cm$^{-1}$. They correspond to $3F_{2g}, 1E_g$, and $1A_{1g}$ Raman-active modes of the Co$_3$O$_4$, as labelled in Fig. 5.10. The phonon symmetries of Raman peaks are caused by the lattice vibrations of the spinel structure, in which Co$^{2+}$ and Co$^{3+}$ cations are situated at tetrahedral and octahedral sites in the cubic lattice. Compared with bulk Co$_3$O$_4$, the peak positions of the five active modes are shifted to lower wave numbers at 9, 22, 15, 25, and 33 cm$^{-1}$, respectively. This phenomenon is attributed to the optical phonon confinement effect in nanostructures that causes uncertainty in the phonon wave vectors and then a downshift of the Raman peaks [44-47].

Fig. 5.11 (a-d) shows the XPS spectra of pure and Ce doped Co$_3$O$_4$ nanoparticles synthesized from microwave assisted route. A certain strong peaks found at 778.9 and 794.8 eV belong to Co 2p$_{3/2}$ and Co 2p$_{1/2}$ levels of Co$_3$O$_4$ nanoparticles for all the three calcined and 10% Ce doped samples shown in Fig. 5.11(a & b). The energy separation of Co 2p spin orbit doublets (2p$_{3/2}$ to 2p$_{1/2}$) is found to be 15.9 eV that matches well with previous reports [48]. Fig. 5.11(b) clearly shows the existence of shakeup satellite peak at 9 eV with the main peak, which concludes that the oxidation states of Co are also the mixed valences of Co$^{2+}$ and Co$^{3+}$. The corresponding peaks for Co 2p are slightly shifted to 2 or 3 eV with previous literature reports which may be due to the presence of Ce ion in lattice sites. Fig. 5.11(c) presents the O 1s level peak exhibited at 529.8 eV for Co$_3$O$_4$ samples calcined at 400 °C, 600 °C and 800 °C. It is also noted from the XPS
spectra that, the Co$_2$O$_4$ sample subjected to higher calcination produces high intense Co 2p and O 1s levels compared to lower calcination temperatures.

![Raman spectra](image)

**Fig. 5.10:** Raman spectra of undoped and Ce doped Co$_2$O$_4$ cubic structures

![XPS spectra](image)

**Fig. 5.11:** XPS spectra of a) Co 2p level of different calcined samples, b) Co 2p level of 10% Ce doped c) O 1s level and d) Ce 3d level of Co$_2$O$_4$ cubic structures
From the XPS spectrum shown in Fig. 5.11(d), the peaks at binding energies of 902.5 and 919.3 eV can be attributed to Ce$^{4+}$ 3d$_{5/2}$ and Ce$^{4+}$ 3d$_{3/2}$, respectively. The peaks at binding energies of 887.9 and 906.1 eV can be attributed to Ce$^{3+}$ 3d$_{5/2}$ and Ce$^{3+}$ 3d$_{3/2}$, respectively. Thus, the mixed valences of Ce$^{3+}$ and Ce$^{4+}$ coexisted in Ce-doped Co$_3$O$_4$ samples.

### 5.3.7 Magnetic Measurements

The conversion of sample dimensions to nanolevel from bulk consisting of antiferromagnetic (AFM) property that may be attributed from the uncompensated surface spins and/or finite size effects [49–51]. In all our samples, the magnetization value sharply increases with the external applied field strength (Fig. 5.12(a–e)). Even though, the observation of non-saturation in M–H, small hysteresis loop exhibited in all the samples represent weak ferromagnetism nature of the Co$_3$O$_4$ nanoparticles and this trend is well suited with previous reports. In general, the magnetization value increases with decreasing particle size and the highest value of magnetization is obtained for 600 °C calcined sample with very low coercive value.

Hence, the origin of week ferromagnetism of Co$_3$O$_4$ nanoparticles is also viewed as super paramagnetic behavior in our cases may be related to uncompensated surface spins and/or finite size or it may also contributed from the spinel structure by local electron hopping [52–54].
Fig. 5.12: Hysteresis loops of Co$_3$O$_4$ using different a) Calciantions, b) Surfactants c) Methods, d) Microwave powers, e) metal doped (M=Ni, Mg, Zn & Fe) and e) Ce doped Co$_3$O$_4$ cubic structures
The inflection point observed in M(H) curve of C8 sample (Fig. 5.12(a)) can be explained by the particles size dependent. This sample has larger particle size due to the high calcinations temperature. As the particles size increased, the surface to volume ratio decreased. So, the contribution from the surface spins are less and at the same time the influence from the weak ferromagnetic state is high which can be seen from the inflection point. The improved magnetization values for CTAB and citric acid added Co3O4 samples are due to their reduced crystallite size of less than 25 nm than hexamine as shown in Fig. 5.12(b). The preparation of Co3O4 sample by microwave method produced less crystallite size of 20 nm which shows higher magnetization value than conventional hydrothermal method(Fig. 5.12(c)) which indicates that microwave method is more suitable than other methods to enhance the magnetic performance of Co3O4 materials.

The magnetization values for the samples prepared from microwave method using different microwave powers are shown in Fig. 5.12(d). The higher microwave powers used samples are showing increased magnetization values due to their improved size/surface modification. In similar way, the reduced crystallite size for increased rare earth (Ce) doped Co3O4 samples show higher magnetization values as shown in Fig. 5.12(e). It is noteworthy that, the increase in saturation magnetization is most significantly influenced by morphology and particle size of nanostructures. The observed results demonstrate that the presence of surfactants and addition of metal / rare earth such as Ni, Mg, Zn, Fe and Ce can be successfully used to improve the magnetic performance of Co3O4 nanostructures especially for magnetic storage applications.
5.4 CONCLUSION

Cubic phase of Co₃O₄ nanostructures were prepared by fast and facile microwave assisted method. XRD pattern revealed the formation of nanosized Co₃O₄ without altering the crystalline nature for the samples prepared with different conditions. SEM analysis revealed the existence of hexagonal stacked plate for CTAB assisted and metal (Ni, Mg, Zn, Fe and Ce) incorporated Co₃O₄ and spherical like morphologies for citric acid added Co₃O₄. The agglomeration of morphological structures was controlled by the addition of dopants into Co₃O₄ lattice sites. The functional and vibration modes of Co₃O₄ nanostructures were analyzed by FTIR and Raman. It is suggested that the addition of surfactants or incorporation of TM and RE metals causes for the size / surface modifications which is found to be an accountable factor for the enhancement of magnetic properties at room temperature revealed from vibrating sample magnetometer.
REFERENCES


