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**A Comparative study on the synthesis of Co-doped manganese ferrite  
[Mn<sub>(1-x)</sub>Co<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5)]  
nanoparticles via microwave assisted and conventional combustion method**

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**Abstract:** As a promising material for soft magnets, cobalt doped manganese ferrite [Mn<sub>(1-x)</sub>Co<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5)] nanoparticles were prepared by two methods (conventional combustion and microwave assisted combustion technique). Nitrates of the constituent elements and urea were respectively used as the oxidizer and fuel to drive the reaction. The effect of microwave irradiation on the phase composition, microstructure, magnetic and optical properties were found to be superior to the samples prepared by conventional method, due to the rapid processing and uniform temperature distribution, throughout the reaction. The X-ray diffraction (XRD) results confirmed the formation of pure and cubic spinel structure. The crystallite size of the nanoparticles was in the range of 19 - 25 nm for those prepared by microwave method. The range was higher for the nanoparticles prepared by conventional method. It was evident from the results of energy dispersive X-ray (EDX) analysis that all the samples were pure, with no change in the composition of the elements present. The grain size of the nanoparticles decreases on the addition of Co<sup>2+</sup> ions. The high resolution scanning electron microscope (HR-SEM) differentiated the decrease in particle size of the nanoparticles by the two different methods. The UV-visible diffuse reflectance spectroscopy (DRS) was recorded to estimate their band gap energy. The magnetic measurements of all the samples were recorded using vibrating sample magnetometer (VSM) at room temperature in 10 kOe. The values of saturation magnetization (M<sub>s</sub>), remanant magnetization (M<sub>r</sub>) and coercivity (H<sub>c</sub>) were obtained from the magnetic studies.

**Keywords:** Co<sup>2+</sup> doped manganese ferrite; microwave combustion; saturation magnetization; X-ray diffraction; structural and magnetic properties.

## Introduction

Transition metal ferrites are the key components for many technological applications, and these functional materials often contain one or more transition-metal elements whose ionic radii and oxidation states are crucial for determining their magnetic, optical and structural properties. The idea of producing such materials allows new fundamental knowledge of properties of the solid state to be developed; for example, much current research is focused on the nanoscale and the effect upon physical properties of the well-defined nanostructured materials. This present study is concerned with the development of versatile synthesis methods for the preparation of cobalt doped manganese ferrite nanoparticles and to study their change in properties.

As a binary metal oxide, manganese ferrite ( $\text{MnFe}_2\text{O}_4$ ) was found to be highly applicative in magnetic devices<sup>1</sup>, drug delivery<sup>2</sup>, supercapacitor<sup>3</sup>, hyperthermia applications<sup>4</sup>, anode materials for lithium-ion batteries<sup>5</sup>, biomedical applications<sup>6</sup>, cancer imaging and therapy<sup>7</sup> etc. Formation of mixed metal oxide like ferrites are highly feasible with manganese, since it has various oxidation states such as I, II and III<sup>8</sup>. Manganese ferrite,  $\text{MnFe}_2\text{O}_4$ , belong to a group of soft magnetic materials characterized by high magnetic permeability, low eddy losses, high Curie temperature and high saturation magnetization<sup>9</sup>. Ferrites involving cobalt has gained its prominence due to its high coercivity ( $H_c$ ), moderate saturation magnetization ( $M_s$ )<sup>10</sup>, good chemical stability and high mechanical hardness<sup>11</sup>. These properties finds its application in the field of medicine<sup>12</sup>, electronic devices<sup>13</sup> and in the complete decomposition of  $\text{CO}_2$ <sup>14</sup>.

A large number of methods have been developed to prepare pure and doped ferrites, such as, solvothermal synthesis<sup>15</sup>, sol-gel auto-combustion method<sup>16</sup>, co-precipitation method<sup>17</sup>, reverse co precipitation method<sup>18</sup>, simple ceramic method<sup>19</sup>, micro emulsion<sup>20</sup>, hydrothermal synthesis<sup>21</sup> and electrochemical method<sup>22</sup>. All these methods have some disadvantages, such as, long time consumption, high energy consumption and the need for a very high calcinations step. Further developments of these methods are restricted to certain extent.

Conventional combustion synthesis is a most common commercial approach for the bulk syntheses of ferrites. It is a convenient, inexpensive, environment friendly and an efficient method for the preparation of ferrites. The process involved is simple and shows high crystallinity of the sample and consumes less processing temperature. This method of synthesizing ferrites has led to pure, ultra fine and narrow size distribution of particles<sup>23</sup>.

Conventional combustion method has been employed to synthesize pure  $\text{CoFe}_2\text{O}_4$  nanoparticles assisted by urea as the fuel<sup>24</sup>. Furthermore, conventional methods has been used to prepare manganese substituted copper ferrite nanoparticles<sup>25</sup>, for the synthesis of Ni-Zr doped barium strontium hexaferrite<sup>26</sup> and conventional-hydrothermal method has been used to prepare Ni and Zn ferrite powder. Moreover, microwave combustion method offers great advantages over the other traditional processing techniques, since the microwave energy interacts with the reactants at the molecular level, due to the rapid and volumetric heating leading to enhanced homogeneity, microstructure, higher yield, better reproducibility and energy saving<sup>27</sup>. It is also characterized by the controlled grain growth, high densification at comparatively lower sintering temperature, shorter soaking duration<sup>28</sup>, enhanced quality and properties of the processed materials<sup>29</sup>.

Microwave processing of materials is a technology that provides a new, efficient and significantly different tool to process the materials or to enhance the performance characteristics of existing materials<sup>29</sup>. Microwave combustion method have been employed to prepare ferrite powders and their composite films<sup>30</sup>. It has been used to synthesize Mg-doped  $\text{ZnFe}_2\text{O}_4$  nanoparticles<sup>31</sup>, for the synthesis of manganese-zinc ferrite nanopowders<sup>32</sup> and in the preparation of  $\text{BaTiO}_3-x\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  samples<sup>28</sup>. In the present study, preparation of Co doped  $\text{MnFe}_2\text{O}_4$  nanoparticles will be investigated using both the conventional combustion method and microwave combustion method. In both the methods, urea is used as the fuel and the precursors are taken in the form of metal nitrates, which acts as the oxidizer. The products from both the methods have been characterized using SEM (scanning electron microscope) to study the morphology; XRD (x-ray diffraction analysis) has been used to evaluate the crystallite structure and the purity of the prepared phase, DRS (diffuse reflectance spectroscopy) to study the band gap energy; and to study the magnetic properties of the samples.

## Experimental

### Materials and characterization

Cobalt doped manganese ferrite  $Mn_{1-x}Co_xFe_2O_4$  ( $0.0 \leq x \leq 0.5$ ) samples were synthesized by microwave combustion method and conventional method. All the precursors used namely cobalt nitrate, manganese nitrate, ferric nitrate and urea were of analytical grade, purchased from MERCK, India in the pure form. Urea is used as the combusting agent in both the methods of preparation.

The metal nitrates of the above mentioned constituents were dissolved in water individually and the solutions were mixed together in the same vessel. An aqueous solution of urea, the combusting agent is added to the above mixture and kept for dissolution by stirring for 30 min using a magnetic stirrer, until a clear solution without any sedimentation is obtained. In microwave combustion method, the clear solution after stirring is subjected to the microwave radiation in the oven, which was set to 900 MHz at 540 W for 12 min. In the conventional method, the clear solution obtained after stirring was heated using a heating mantle at 120°C for 1h. The resultant samples were cooled and thermally treated at 900°C for 2h, in a high temperature furnace.

The microwave prepared samples were denoted as MMn, MCo1, MCo2, MCo3, MCo4 and MCo5 (where MMn represents pure  $MnFe_2O_4$ , MCo1 represents  $Mn_{0.9}Co_{0.1}Fe_2O_4$ , MCo2 represents  $Mn_{0.8}Co_{0.2}Fe_2O_4$ , MCo3 represents  $Mn_{0.7}Co_{0.3}Fe_2O_4$ , MCo4 represents  $Mn_{0.6}Co_{0.4}Fe_2O_4$  and MCo5 represents  $Mn_{0.5}Co_{0.5}Fe_2O_4$ ) with respect to the ratio of cobalt nitrate added.

The samples prepared by conventional method were denoted as CMn, CCo1, CCo2, CCo3, CCo4 and CCo5 (where CMn represents pure  $MnFe_2O_4$ , CCo1 represents  $Mn_{0.9}Co_{0.1}Fe_2O_4$ , CCo2 represents  $Mn_{0.8}Co_{0.2}Fe_2O_4$ , CCo3 represents  $Mn_{0.7}Co_{0.3}Fe_2O_4$ , CCo4 represents  $Mn_{0.6}Co_{0.4}Fe_2O_4$  and CCo5 represents  $Mn_{0.5}Co_{0.5}Fe_2O_4$ ) with respect to the ratio of cobalt nitrate added.

## Results and Discussion

### Characterization

Cobalt doped manganese ferrite  $Mn_{1-x}Co_xFe_2O_4$  ( $0.0 \leq x \leq 0.5$ ) samples, MMn, MCo1, MCo2, MCo3, MCo4, MCo5, CMn, CCo1, CCo2, CCo3, CCo4 and CCo5 were subjected to XRD analysis with Rigaku Ultima X-ray diffraction unit (Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ )) to explore the structural properties. The scanning electron microscope was used to examine the particle morphology using a JEOL JSM6360 high resolution scanning electron microscope (HR-SEM) along with the energy dispersive X-ray analysis (EDX). The magnetic properties of the samples were investigated using vibrating sample magnetometer (VSM) (PMC MicroMac 3900) equipped with 1 Tesla magnet. The UV-Visible diffuse reflectance spectrum (DRS) was recorded using Cary 100 UV-Visible spectrophotometer to estimate their band gap energy.

### Structural analysis

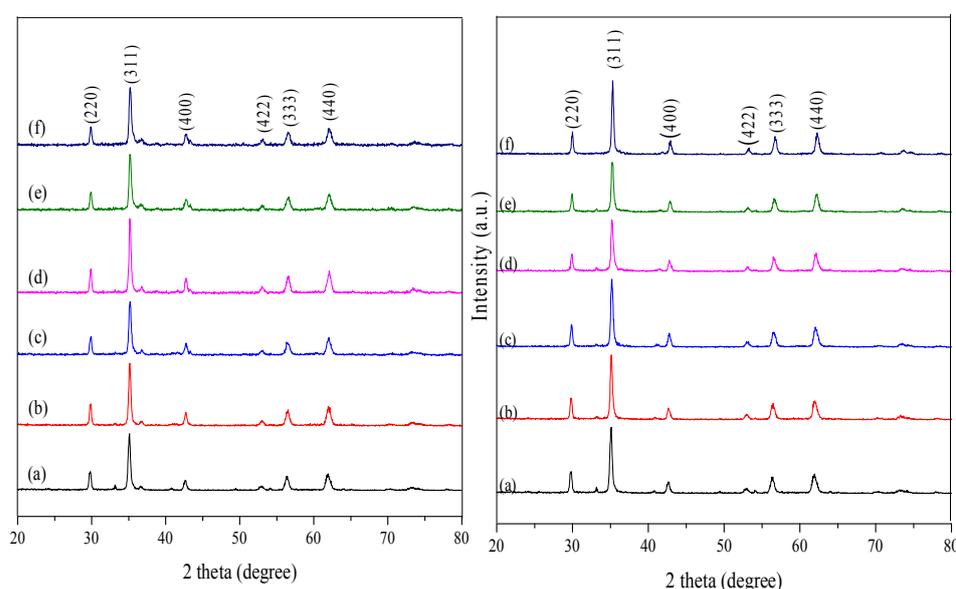
The XRD pattern of the prepared samples is given in Figure 1 and Figure 2. Figure 1 showed the XRD pattern of the samples prepared by microwave combustion method and Figure 2 displayed the XRD pattern of the samples prepared by the conventional method. All the reflection peaks identified correspond to the spinel structure and were indexed in good agreement with the referred database of JCPDS Card No: 74-2403[9]. The peaks could be indexed as (111), (220), (311), (400), (333) and (440), which are characteristics of a single-phase cubic spinel structure. The intensity of the main diffraction peak at the plane (311) was considered as a measure of its degree of crystallinity. The average crystallite size of all the samples was calculated by using the Debye-Scherrer formula

The calculated values are given in Table 1. All the samples were found to exhibit cubic structure with Fd-3m space group. The average crystallite size was found to be 23.04 nm and 43.56 nm for the samples prepared by microwave and conventional method, respectively. An increase in the crystallite size of the samples prepared by conventional method is the consequence of calcining the samples at 900°C, because conventional method is a high-energy consuming and require long reaction times. The exposure of the crystallites to high temperature for a long duration has caused to an increase in the size of the crystallites that takes place owing to solid-state diffusion<sup>9</sup>. The XRD peaks obtained show an increased sharpness with the calcinations temperature and thus enhancing the crystallization of the ferrite phase produced.

In the samples prepared by microwave combustion method the refined values of the crystallite size increases linearly with increasing the cobalt concentrations as shown in Figure 1. The samples were subjected to microwave radiation only for 12 min and the calcinations temperature was 700 °C which led to the formation of  $Mn_{1-x}Co_xFe_2O_4$  nanoparticles. The increase in the crystallite size with  $Co^{2+}$  content may be attributed to the different cationic radii<sup>33</sup>.

The lattice parameter (a) for all the compositions was calculated from the diffraction planes using the formula, where a is the lattice constant, d, interplanar distance and h, k, l are the Miller indices.

As the  $Co^{2+}$  content increases from 0.1 to 0.5, the value of the lattice parameter 'a' decreases from 8.477 to 8.429. (vegard's law)<sup>33</sup>. This decrease in the value of 'a' may be attributed to the quantum confinements in nanomaterials, due to the replacement of  $Mn^{2+}$  ( $r_{Mn^{2+}} = 0.83\text{\AA}$ ) ions from octahedral site by smaller  $Co^{2+}$  ( $r_{Co^{2+}} = 0.78\text{\AA}$ ) ions. The similar kind of behavior in the lattice parameter is observed in the samples prepared by the conventional method. However, the crystallite size increases with increasing the temperature in conventional combustion method.



**Fig 1.** XRD patterns of (a)MMn (b)MCo1 (c)MCo2 (d)MCo3 (e)MCo4 and (f)MCo5

**Fig 2.** XRD patterns of (a)CMn (b)CCo1 (c)CCo2 (d)CCo3 (e)CCo4 and (f)CCo5

### Scanning electron microscopy (SEM) studies

The HR-SEM images of conventionally prepared  $Mn_{1-x}Co_xFe_2O_4$  samples and that prepared by microwave method are shown in Figure 3. Figure 3 (a-d) shows relatively well defined nanoparticles when compared with those in Figure 3 (e-h). The size of the nanoparticles obtained from the microwave method was in the range of 50-100 nm on an average.

The particle size in the conventional method of preparation is nearly 100-200 nm. Decrease in the particle size suggest the microwave combustion method to be the efficient method to prepare  $Mn_{1-x}Co_xFe_2O_4$  samples. The compositional analysis of the  $Mn_{1-x}Co_xFe_2O_4$  samples was observed using energy-dispersive X-ray spectra (Figure 4). The spectrum shows the peaks corresponding to Mn, Co, Fe and O. The result confirms the purity of the samples with no additive impurities. From the results, it can be observed that the experimental values of atomic percentage matches with the stoichiometry in preparation.

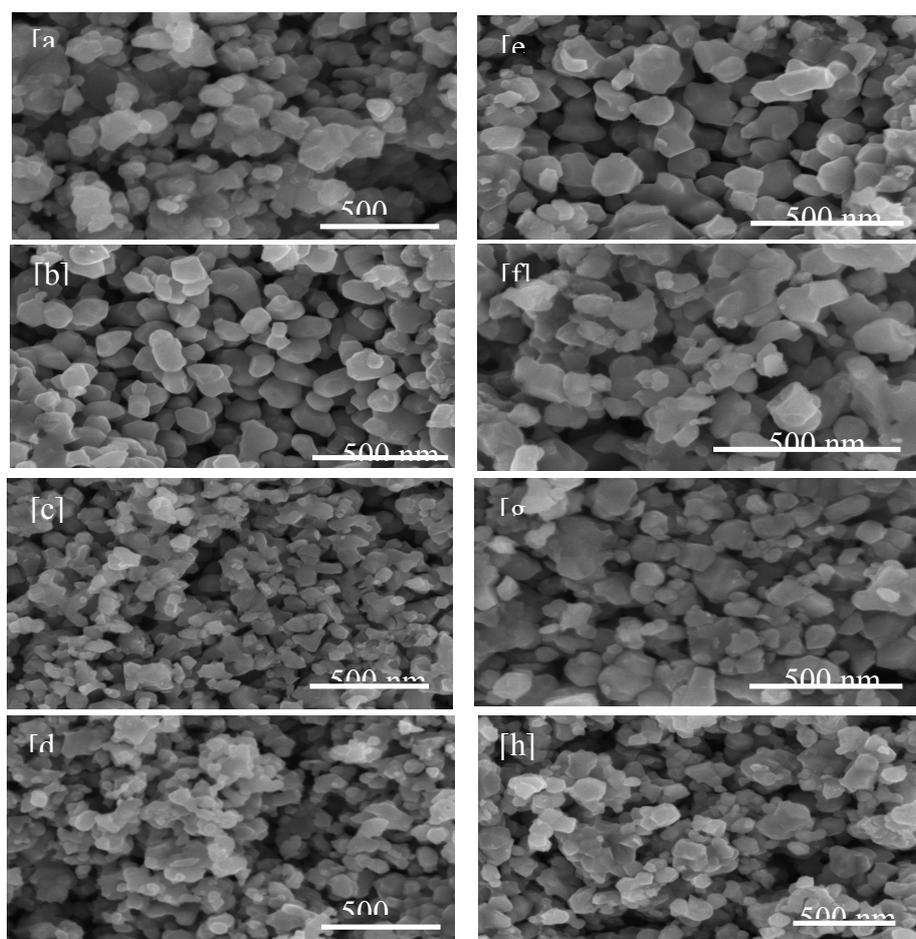
### Magnetic Properties

The magnetic properties, such as, saturation magnetization ( $M_s$ ), remanant magnetization ( $M_r$ ) and coercivity ( $H_c$ ) are the important parameters for studying the magnetic behavior of ferrite samples. The value of saturation magnetization for  $Mn_{1-x}Co_xFe_2O_4$  samples prepared by the conventional method and microwave combustion method are shown in

**Table 1** Lattice parameter, crystallite size and band gap of  $Mn_{1-x}Co_xFe_2O_4$  ( $x=0.0, 0.1, 0.2, 0.3, 0.4$  and  $0.5$ ) samples Figure 5.

Sample Code	Lattice parameter (Å)		Crystallite size, L (nm)		Band gap (eV)	
	Conventional	Microwave	Conventional	Microwave	Conventional	Microwave
$MnFe_2O_4$	8.457	8.477	39	24	2.10	3.00
$Mn_{0.9}Co_{0.1}Fe_2O_4$	8.466	8.478	80	19.62	2.02	2.6
$Mn_{0.8}Co_{0.2}Fe_2O_4$	8.476	8.459	79	21.2	1.97	2.3
$Mn_{0.7}Co_{0.3}Fe_2O_4$	8.451	8.461	40	22.48	1.93	2.2
$Mn_{0.6}Co_{0.4}Fe_2O_4$	8.459	8.449	58	25.39	1.86	2.8
$Mn_{0.5}Co_{0.5}Fe_2O_4$	8.455	8.429	42	25.6	1.80	2.9

The plots have shown that the saturation magnetization ( $M_s$ ) prepared by microwave combustion method initially decreases with an increase in the concentration of dopant  $Co^{2+}$  ions and then increases with higher concentration of  $Co^{2+}$  ions. This may be attributed to the fact that  $Fe^{3+}$  ions (magnetic moment= $5\mu_B$ ) are replaced by lesser magnetic metal ion  $Co^{2+}$  (magnetic moment= $3\mu_B$ ) in the octahedral B-sites of the ferrite sublattice<sup>34</sup>. From the spectroscopic measurements, it was found that  $Co^{2+}$  ions have strong site preference for octahedral sites, while  $Fe^{3+}$  and  $Mn^{2+}$  have no particular preference for either coordination<sup>35</sup>. The values are given in Table 2. Samples prepared by conventional method also follow the same trend in the saturation magnetization behavior.

**Figure 3.** HR-SEM images of (a) MMn (b) MCo1 (c) MCo3 (d) MCo5 (e) CMn (f) CCo1 (g) CCo3 (h) CCo5 sample.

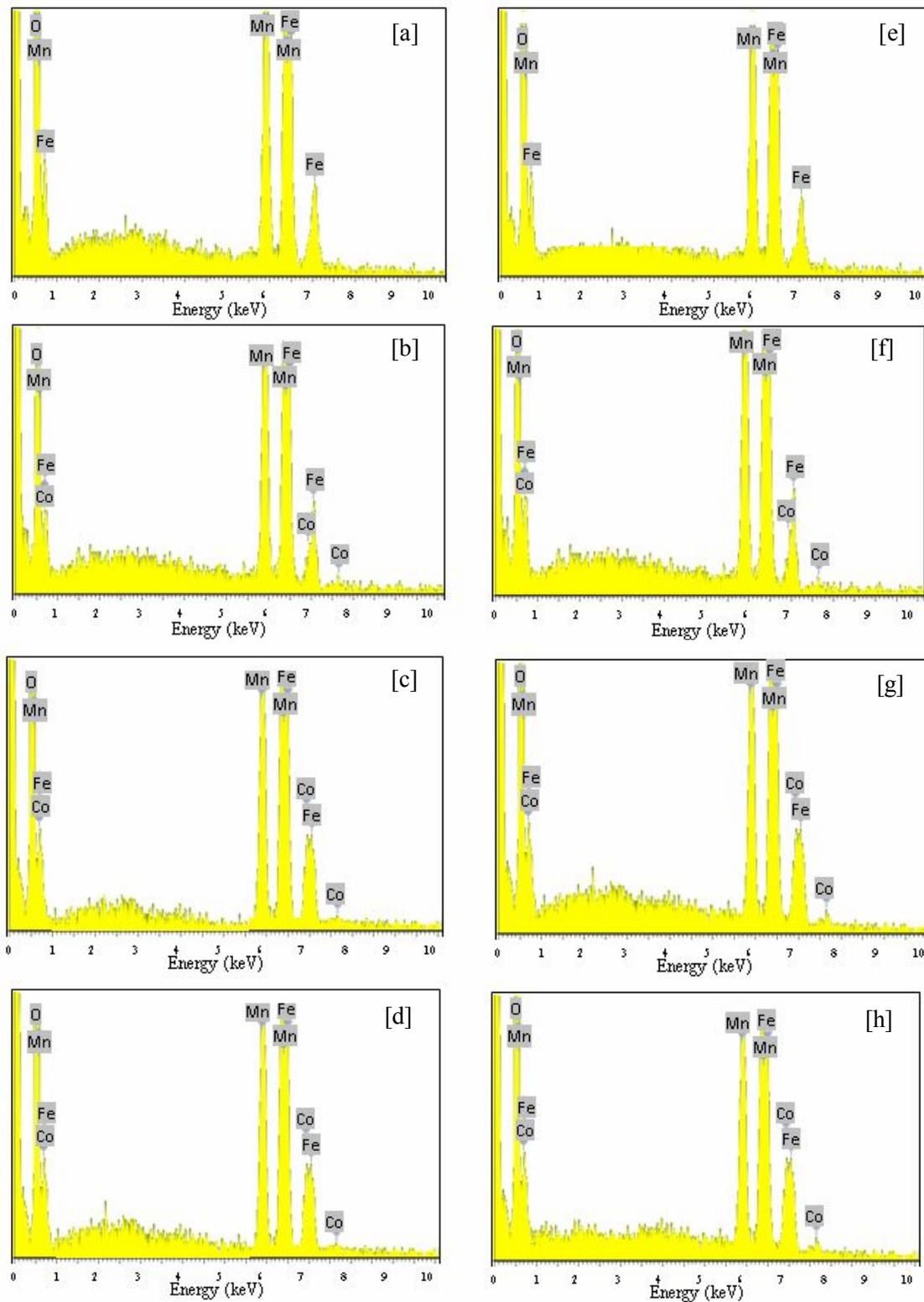
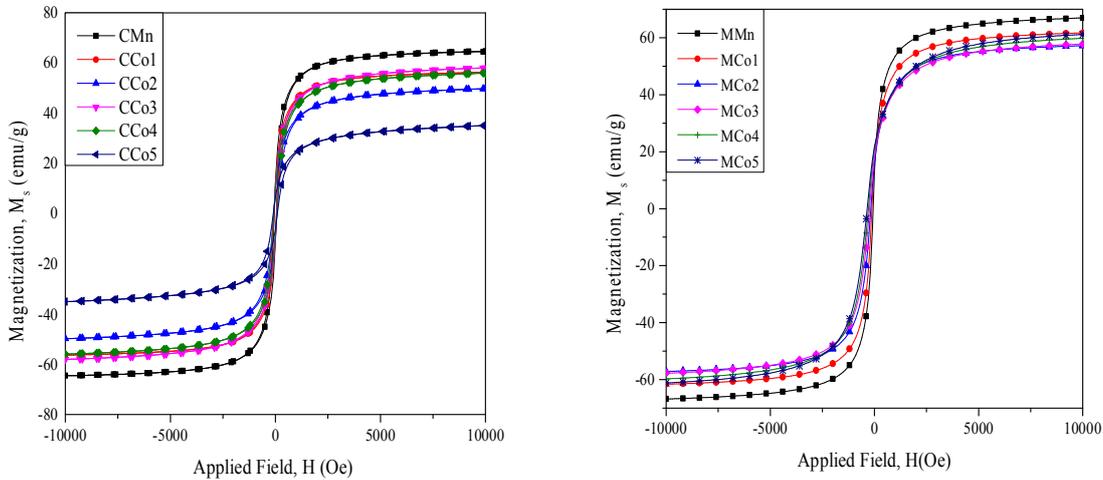


Figure 4.EDX spectra of(a) MMn (b) MCo1 (c)MCo3 (d) MCo5 (e) CMn (f) CCo1 (g)CCo3 (h) CCo5 samples

Table 2 :Variation of coercivity ( $H_c$ ), remanant magnetization ( $M_r$ ) andsaturationmagnetization( $M_s$ )of $Mn_{1-x}Co_xFe_2O_4$ ( $x=0.0, 0.1, 0.2, 0.3, 0.4$  and  $0.5$ )samples.

Sample Code	$H_c$ (Oe)		$M_r$ (emu/g)		$M_s$ (emu/g)	
	conventional	microwave	conventional	Microwave	conventional	microwave
MnFe <sub>2</sub> O <sub>4</sub>	51.33	58.45	11.75	11.45	66.89	64.62
Mn <sub>0.9</sub> Co <sub>0.1</sub> Fe <sub>2</sub> O <sub>4</sub>	59.31	118.2	15.60	16.84	61.67	56.34

$Mn_{0.8}Co_{0.2}Fe_2O_4$	79.80	170.5	15.61	16.92	57.17	49.81
$Mn_{0.7}Co_{0.3}Fe_2O_4$	72.83	235.6	17.98	19.14	57.78	58.08
$Mn_{0.6}Co_{0.4}Fe_2O_4$	99.26	290.7	20.54	21.42	59.77	61.45
$Mn_{0.5}Co_{0.5}Fe_2O_4$	110.32	349.3	21.62	23.57	61.17	63.54



**Figure 5. Magnetic hysteresis loops of (a) MMn (b) MCo1 (c) MCo2 (d) MCo3 (e) MCo4 (f) MCo5 (g) CMn (h) CCo1 (i) CCo2 (j) CCo3 (k) CCo4 and l) CCo5 samples**

The increase in coercivity for the  $Mn_{1-x}Co_xFe_2O_4$  samples with an increase in  $Co^{2+}$  content might be due to the increase in magnetic crystalline anisotropy<sup>36</sup>, which is correlated with spin-orbital contribution. Even though, the same behavior is exhibited by the samples prepared by conventional method, the range of increase in coercivity for conventional method is comparatively lesser than the microwave method. This may be due to the difference in the method of preparation and calcinations temperature.

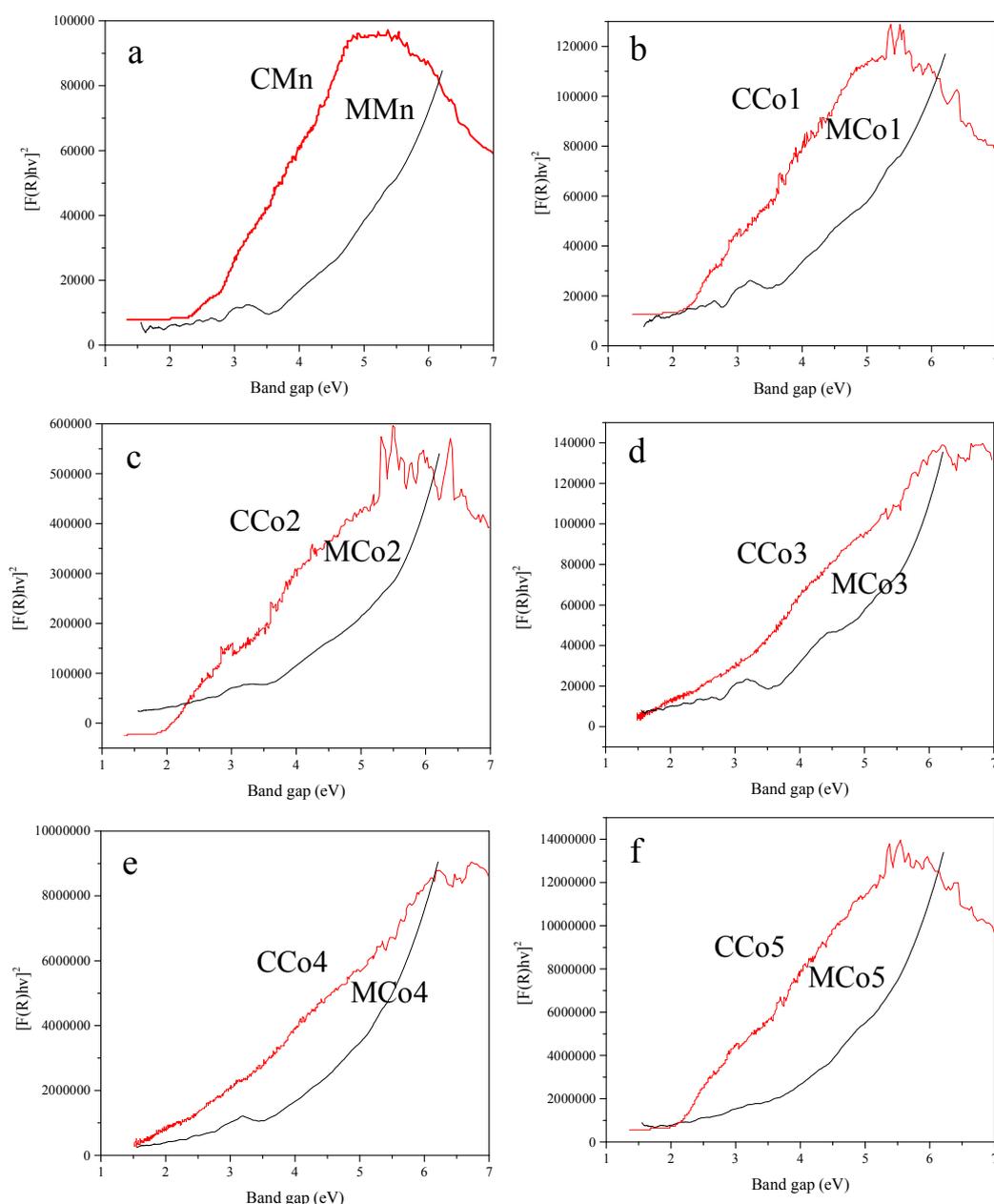
### Diffuse reflectance spectroscopy (DRS) studies

UV-Visible diffuse reflectance spectroscopy measurements for the  $Mn_{1-x}Co_xFe_2O_4$  samples prepared by conventional and microwave method were carried out to study the optical behavior of the samples. For powder samples, the absorption coefficient ( $\alpha$ ) is calculated from the UV-Visible diffuse reflectance spectroscopy measurements. Kubelka-Munk function is used to calculate the band gap ( $E_g$ ) of the samples in eV. All the samples display the optical properties at the visible region, which is due to the band-gap transition of the  $Mn_{1-x}Co_xFe_2O_4$  samples and is in agreement with the black color of the samples. Kubelka-Munk function  $F(R)$  is directly proportional to the absorption coefficient ( $\alpha$ ) and the value is estimated from the following equation,

$$F(R) = \alpha = \frac{(1 - R)^2}{2R}$$

where,  $F(R)$  is Kubelka-Munk function,  $\alpha$ , the absorbance, and  $R$ , the reflectance.

$[F(R)h\nu]^2$  vs  $h\nu$  is plotted from which the band gap values of the samples are calculated by extrapolating the intercept (Figure 6 a-f). The calculated band gap values of the  $Mn_{1-x}Co_xFe_2O_4$  samples prepared by microwave combustion method are 3.0, 2.6, 2.3, 2.2, 2.8 and 2.9 eV respectively (Figure 6 and Table 1). From the results, it can be understood that the band gap value decreases, as the doping increases. It is similar to the results obtained from XRD and SEM studies. The band gap value decreases with an increase in  $Co^{2+}$  doping till MCo3. Further, doping of  $Co^{2+}$  in the  $MnFe_2O_4$  matrix has led to the increase in band gap value. For the samples prepared by the conventional method, a similar decrease in band gap value is obtained, but the value of band gap is lesser, when compared to the one prepared by the microwave method. The value ranges from 2.10-1.80 eV respectively.



**Figure 6. UV-visible diffuse reflectance spectra of (a) MMn&CMn(b) MCo1&CCo1 (c) MCo2&CCo2 (d) MCo3&CCo3 (e) MCo4 &CCo4 (f) MCo5 &CCo5 samples**

## Conclusion

Great efforts have been made for the efficient preparation of Co doped manganese ferrite  $Mn_{1-x}Co_xFe_2O_4$  ( $0.0 \leq x \leq 0.5$ ) samples, to enhance its magnetic, optical, morphological and structural properties. Microwave combustion method of preparation was found to show better results when compared to the samples prepared by the conventional method. The X-ray diffraction analysis showed an increase in the crystallite size for the conventional method and microwave method showed a lesser value in the crystallite size. SEM images revealed a well define nanoparticles with smaller particle size for the samples prepared by microwave method. These samples showed higher saturation magnetization ( $M_s$ ) and the band gap energy from the DRS measurements was also found to be higher than the ones prepared by the conventional method.

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