

# Synthesis and Study on Structural, Morphological and Magnetic properties of nanocrystalline Manganese Oxide

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**Abstract:**  $Mn_3O_4$  nanoparticles were prepared by co-precipitation method followed by annealing of samples at 300 °C for 2 hours. The samples were characterized to find the structural, functional, optical, morphological, compositional and magnetic properties by PXRD, FTIR, Micro-Raman, HRSEM, TEM, XPS, EDX and VSM respectively. Structural studies by PXRD indicate that the annealing has strongly influenced the phase transition showing two coexisting phases of  $Mn_2O_3$  and  $Mn_3O_4$ . Micro-Raman spectra showed the presence of  $A_{1g}$  mode of vibration corresponding to  $Mn_3O_4$  phase. Magnetic studies of the as synthesized  $Mn_3O_4$  nanoparticles depict paramagnetic behavior at room temperature.

**Keywords:** manganese oxide, co precipitation, magnetic properties

## 1. INTRODUCTION

In recent past, considerable research attention is paid on Mn based compounds as it has many interesting properties that can be tailored for numerous applications.  $Mn_3O_4$  is an important transition metal oxide due to its extensive applications in magnetic [1], electrochemical [2], Li ion batteries [3], catalytic applications [4], supercapacitors [5] and dilute magnetic semiconductor [6].  $Mn_3O_4$  nanoparticles have been synthesized in several methods like hydrothermal [7], combustion method [8], microwave assisted solution method [9], and co precipitation method [10]. In this report, we have attempted to optimize  $Mn_3O_4$  nanoparticles by facile co-precipitation method as it is simple and cost effective technique. As synthesized nanoparticles were annealed to 300 °C and their structural, morphological, functional, compositional and magnetic properties were compared.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Synthesis of Manganese Oxide Nanoparticles

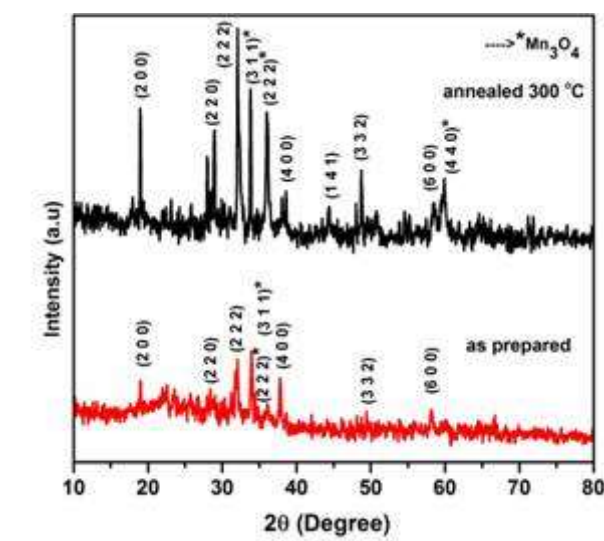
All chemicals used were of AR grade and was used without further purification. A simple chemical co precipitation method was employed to synthesis  $Mn_3O_4$  nanoparticles. 1M of  $MnSO_4 \cdot H_2O$  was dissolved in de-ionized water. 2M of NaOH was added drop wise to this solution and pH was maintained at  $11 \pm 0.2$  by adding ammonia. Solution was stirred continuously under constant temperature (60 °C) for 2 hours for precipitation of nanoparticles. Then precipitated particles was collected and washed with de-ionized water 2 to 3 times and dried in hot air oven at 100 °C for 12 hours. As synthesized particles was annealed at 300 °C for 2 hours.

## 3. RESULTS AND DISCUSSION

### 3.1 Structural Studies

Figure 1 show the powder X-ray diffractograms of as synthesized and annealed nanoparticles, which reveals the presence of mixed phases of  $Mn_3O_4$  and  $Mn_2O_3$ . PXRD pattern of as synthesized nanoparticles show predominant peak with reflection (311) at 34.06° which indicates the presence of  $Mn_3O_4$  phase with cubic structure, whereas annealed sample shows predominant peak with reflection (222) at 32.45° which can be assigned to  $Mn_2O_3$  phase with cubic structure. The reflections (222) at 36.06° and (440) at 60.24° can be assigned to  $Mn_3O_4$  phase. These values are in

good agreement with JCPDS card # 040-732. The peaks with reflection (200) at 19°, (220) at 29°, (222) at 32.45°, (400) at 37.9°, (332) at 44.52° and (600) at 58.29° belongs to  $Mn_2O_3$  phase with cubic structure. These peaks are well matched with JCPDS card # 89-4836. Aroused peak intensity of annealed nanoparticles is due to the increase in crystallinity. Due to annealing, there is shift in peak to (222) which is the crystallographic plane indicating the phase change to  $Mn_2O_3$  and this may be due to oxidation of  $Mn_3O_4$  to  $Mn_2O_3$  begins at as low as temperature at 300°C [11-12].



**Figure 1. PXRD diffractograms of as synthesized and annealed mixed phases of  $Mn_3O_4$  nanoparticles.**

The microstructural parameters like crystallite size, microstrain, dislocation density and lattice strain [13] were calculated and tabulated in tables 1&2. It is observed that the crystallite size increased for annealed nanoparticles, while the micro strain and dislocation density were decreased. This depicts increase in crystallinity of nanoparticles. Annealing has showed a significant effect in the structural properties of manganese oxide.

### 3.2 Compositional Studies

Figure 2 shows XPS survey spectrum scanned in the binding energy range between 0 to 1100 eV for as synthesized  $Mn_3O_4$  nanoparticles to collect chemical composition and electronic

states data at surface of the samples. Inset picture shows narrow window scan of Mn 2p state. The survey spectrum shows the presence of Mn, C and O with the presence of no other impurities. The C 1s (284.5 eV) peak was used for the calibration of the spectrum as internal reference. Electronic states of Mn 3s, O 1s, Mn 2p and Mn 3p are well matched with earlier reported values [2]. The peak at 642.7 eV can be assigned to Mn 2p<sub>3/2</sub> corresponding to Mn<sup>3+</sup> and 48 eV can be assigned to 3p<sub>3/2</sub> electronic state [14]. Spin orbit splitting between Mn 3p<sub>1/2</sub> and Mn 2p<sub>3/2</sub> is 11.8 eV which is nearer to literature reports [7]. The binding energies at the Mn 2p<sub>3/2</sub> and Mn 2p<sub>1/2</sub> peaks agree well with that of reported for Mn<sub>3</sub>O<sub>4</sub> indicating oxidation state for Mn [5].

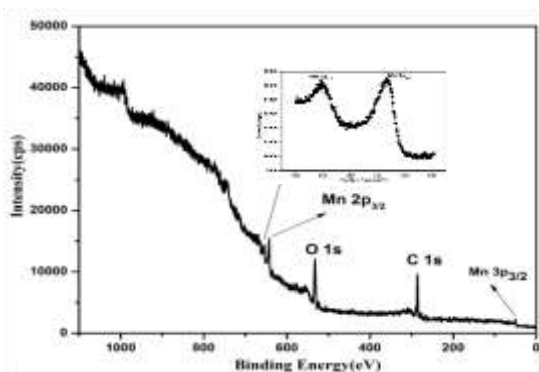
Figure 3 (a&b) shows EDX spectra of as synthesized and annealed nanoparticles. It indicates the presence of Mn and O with the presence of no other impurities.

**Table 1. Lattice parameters of as synthesized and annealed Mn<sub>3</sub>O<sub>4</sub> nanoparticles**

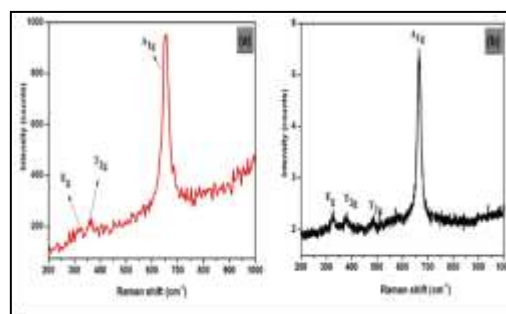
Sample	Lattice Parameter (Å)	Volume (Å <sup>3</sup> )	lattice distortion (Å) V - V <sub>0</sub>
As-synthesized	8.7566	671.428	12.92
Annealed	8.7887	678.850	20.35

**Table 2. Microstructural parameters of as synthesized and annealed Mn<sub>3</sub>O<sub>4</sub> nanoparticles**

Samples	Crystallite size (nm) D=0.9λ/βCosθ	Dislocation density (10 <sup>15</sup> lines/m <sup>2</sup> ) δ=1/D <sup>2</sup>	Micro strain (lines <sup>-2</sup> m <sup>-4</sup> ) ε=βCosθ/4
As synthesized	31.7	0.996	0.0011
Annealed	91.6	0.119	0.0004



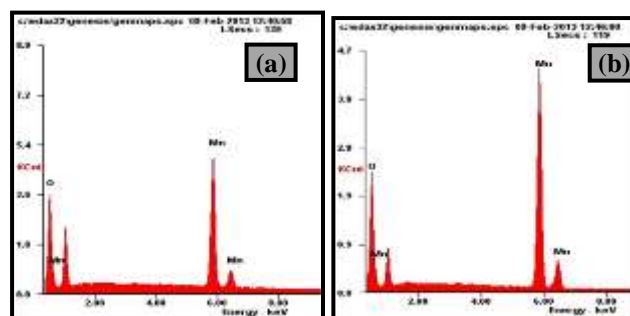
**Figure. 2 XPS spectrum of as synthesized Mn<sub>3</sub>O<sub>4</sub> nanoparticles. Inset**



**Figure. 3 EDS spectra of (a) as synthesized and (b) annealed Mn<sub>3</sub>O<sub>4</sub> nanoparticles**

### 3.3 Functional Studies

The Raman scattering measurements were performed using the 514.5nm excitation line from Ar<sup>+</sup> laser. Figure 4 (a&b) shows the micro-Raman spectra of as synthesized and annealed nanoparticles respectively. As synthesized nanoparticles exhibits three phonon peaks at (doubly degenerate) T<sub>2g</sub> symmetry mode at 366 cm<sup>-1</sup>, E<sub>g</sub> symmetry mode at 320 cm<sup>-1</sup> and a single degenerate A<sub>1g</sub> symmetry mode at 654 cm<sup>-1</sup>. The band corresponding to 654 cm<sup>-1</sup> is very close to 655cm<sup>-1</sup> which is due to the stretching vibration of Mn-O in Mn<sub>3</sub>O<sub>4</sub> [7]. Annealed nanoparticles shows four phonon peaks same as synthesized particles with one extra band T<sub>2g</sub> symmetry mode at 487 cm<sup>-1</sup> which may be due to the out of plane bending mode of Mn<sub>2</sub>O<sub>3</sub> phase. Presence of mixed phase of Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub> is confirmed from these peaks. Also peak intensity of annealed nanoparticles is lesser than that of as synthesized particles. This may be due to increase in crystallite size for annealed nanoparticles which can be explained using phonon confinement effect as reported earlier by Jian Zuo et al [27].

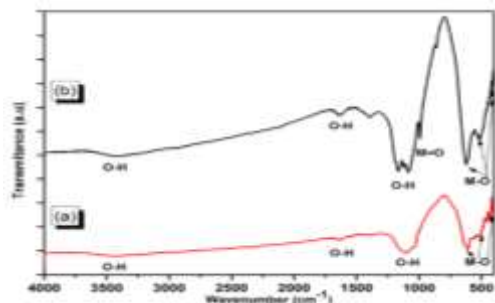


**Figure. 4 Raman spectra of (a) as synthesized and (b) annealed Mn<sub>3</sub>O<sub>4</sub> nanoparticles.**

FTIR spectra for as synthesized and annealed nanoparticles are shown in figure 5(a&b). In the region 400 to 700 cm<sup>-1</sup>, the bands observed at 429 cm<sup>-1</sup>, 458 cm<sup>-1</sup>, 513 cm<sup>-1</sup> and 609 cm<sup>-1</sup> corresponds to the Mn-O vibrations ascribed to the stretching modes of octahedral and tetrahedral sites of Mn<sub>3</sub>O<sub>4</sub> [16]. The bands at 1110 cm<sup>-1</sup> and 1633 cm<sup>-1</sup> are due to the O-H bending vibrations along with Mn [17]. The broad absorption peak at 3443 cm<sup>-1</sup> indicates the presence of hydroxide group. Annealed nanoparticles exhibits an extra peak observed at 995 cm<sup>-1</sup> which may be attributed to M=O vibration of Mn<sub>2</sub>O<sub>3</sub>.

### 3.4 Morphological Studies

HRSEM micrographs of as synthesized and annealed nanoparticles are shown in figure 6(a-c & d-f), which shows irregular shaped disk like morphology with average particle size of about 155 nm. Annealed nanoparticles also exhibit similar morphology with average particle size of about 400 nm.



TEM micrograph (figure 7) of as synthesized nanoparticles was also taken as supporting information. It confirms similar morphology with particle size of 155 nm.

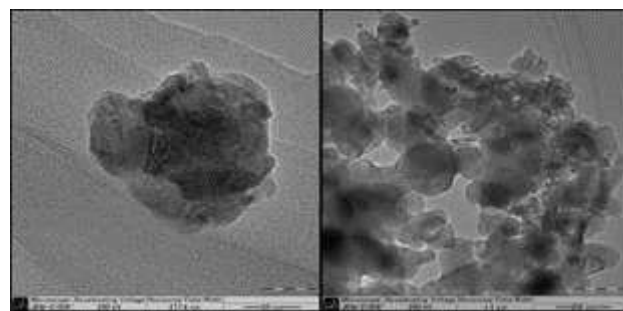


Figure 7. TEM micrographs of as synthesized  $Mn_3O_4$  nanoparticles

### 3.5 Magnetic studies

Magnetic behaviors of as synthesized and annealed  $Mn_3O_4$  nanoparticles are shown in figure 8. This magnetic study was carried out in room temperature with maximum magnetic field at 15 KOe. Both as synthesized and annealed  $Mn_3O_4$  nanoparticles exhibit paramagnetic behavior. The maximum magnetizations observed were 0.2864 emu/g and 0.5347 emu/g for as synthesized and annealed nanoparticles at maximum field. Magnetic ordering of annealed samples is increased with increase in crystallinity of the samples. [19]

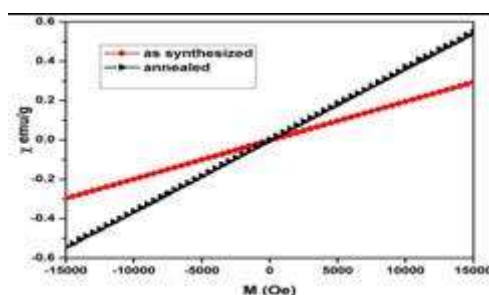


Figure 8. Room temperature magnetization curves of as synthesized and annealed  $Mn_3O_4$  nanoparticles

Figure 5 FTIR spectra of (a) as synthesized and (b) annealed  $Mn_3O_4$  nanoparticles

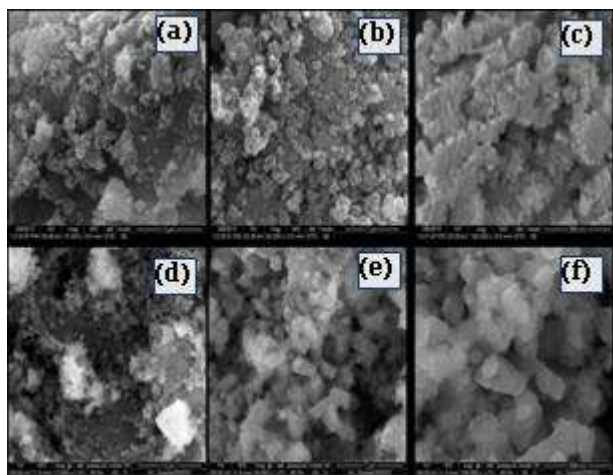


Figure 6. SEM micrographs of (a-c) as synthesized and (d-f) annealed  $Mn_3O_4$  nanoparticles

## 4. CONCLUSION

$Mn_3O_4$  nanoparticles were synthesized by co-precipitation method and their annealing effect was reported. PXRD revealed mixed phases of  $Mn_3O_4$  and  $Mn_2O_3$ . Annealing of nanoparticles at 300 °C has favored the growth orientation towards  $Mn_2O_3$  phase due to oxidation of  $Mn_3O_4$ . Increased peak intensity and decreased microstrain and dislocation density indicates the increase in crystallinity for annealed samples. XPS spectra proved the presence of Mn and O with presence of no other impurities. EDS also confirmed the composition of the samples. HRSEM micrographs showed irregular shaped plates with average particle size of 155 nm for as synthesized particles and 400 nm for annealed particles. TEM micrograph further confirmed similar morphology with particle size almost same as 155 nm. Functional studies were carried out using micro Raman and FTIR. Various bending and stretching modes of Mn-O and O-H groups were analyzed from these spectroscopic studies. Room temperature magnetic studies confirmed that the paramagnetic behavior of  $Mn_3O_4$  nanoparticles improved for annealed samples due to increase in crystallinity.

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