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Rapid microwave assisted synthesis of Mn_2O_3 and Co_3O_4 nanoparticles and their structural, optical and magnetic properties

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Abstract - *The Mn_2O_3 and Co_3O_4 nanoparticles were synthesized by rapid microwave assisted method and as synthesized samples were further annealed at 550 ^oC and the samples were subjected to analyze structural, optical and magnetic properties. Structural properties of the nano particles were characterized by using X-ray diffractometry. XRD pattern revealed that the existence of Mn_2O_3 with body centered cubic structure and Co_3O_4 with face centered cubic structure. The FTIR spectra confirmed the presence of Mn-O stretching vibration mode at 523 and 575 cm^{-1} and absorption bands appeared at 567 and 647 cm^{-1} were attributed to Co-O stretching and O-Co-O bridging vibration modes. The Raman bands of Mn_2O_3 were assigned at 368, 483 and 652 cm^{-1} which attributed to the out-of-plane bending modes of Mn_2O_3, asymmetric stretching of bridge oxygen species of Mn-O-Mn and symmetric stretching of Mn_2O_3 groups respectively. Further, major Raman bands of Co_3O_4 appeared at 670 cm^{-1} is attributed to characteristic of the octahedral site and other three modes are likely related to the combined vibration of tetrahedral site and octahedral oxygen motions of Co_3O_4. The PL spectra exhibited strong blue emission band at 489 and 488 nm and weak defect-related green emission band at 512 and 505 nm for Mn_2O_3 and Co_3O_4. The magnetic properties were studied by vibrating sample magnetometer (VSM) in both samples at an ambient temperature and the M (H) curves of Co_3O_4 exhibit ferromagnetic nature and Mn_2O_3 shows antiferromagnetic behavior. From these results, both materials are more suitable for magnetic applications.*

Keywords: *Mn_2O_3, Co_3O_4, Microwave oven, XRD, VSM.*

I. INTRODUCTION

Recently, the transition metal oxides nanomaterials have been attracted with keen interest in many areas of physics, chemistry, material science and environment. The beauty of nanomaterials lies in their higher surface to volume ratio compared to bulk material with the same chemical composition. Microwave assisted method is one of the promising technique to synthesis of nano structured materials because of it has numerous advantages like simple, cost effective, rapid and uniform volumetric heating compared to conventional heating method. In microwave synthesis, size and morphology of the nanoparticles can be easily controlled by the addition of solvent, heat and time. Among the different type of functional materials, the manganese and cobalt oxides are the most attractive inorganic compounds and these can be used in wide range of applications such as in the fields of magnetic, optical, catalysis, data storage, biosensor, and energy storage devices due to their excellent physical and chemical properties [1-4]. The present work deals with the rapid synthesis of Mn_2O_3 and Co_3O_4 nanoparticles and elucidation of structurural properties by XRD Rietveld refinement method. The three dimensional crystallography structure of synthesized particles was designed by the use of VESTA software and optical and magnetic properties were also investigated.

II. EXPERIMENTAL PROCEDURE

All chemicals used in the experiment are analytical grade. In a typical procedure, $MnCl_2.4H_2O$ (1mol) and $CoCl_2.4H_2O$ (1mol) were taken as source materials. Then, mixed with 60 ml deionized (DI) water separately using a magnetic stirrer for 15 min at room temperature to form homogeneous solution. Following that, 5 ml ammonia (NH_3) solution was slowly added drop wise in the above solutions to maintain the pH at around 10. Then, solutions were continouesly stirred for 30 min. The resultant solution was then transferred to polypropylene-capped autoclave bottles of 250 ml capacity and then subjected to microwave radiation with the power of 500 W for 10 min by using a microwave oven that works with a frequency of 2.45 GHz. After the completing the reaction process, the autoclave bottles were cooled down to room temperature and the precipitate was washed with deionized water and ethanol for several times to remove soluble ions. Further, the precipitate was dried at 80 ^{0}C in an hot air oven for 12 h. Finally, as-prepared powders were annealed at 550 ^{0}C under air atmosphere for 4 h to obtain Mn_2O_3 and Co_3O_4 nanoparticles.

III. RESULTS AND DISCUSSION

Fig. 1 (a) & (b) shows the XRD patterns of Rietveld refinement fitted Mn_2O_3 and Co_3O_4 nanoparticles. It can be seen from the figure that the XRD Rietveld refinement pattern of both samples have exactly matched with the standard reference to observed diffraction peaks and the short vertical bars indicate the position of Bragg reflection for the respective planes.Typical major diffraction peak appeared at $2\theta \approx 32.93$ which corresponds to (2 2 2) plane and some

other series of peaks at 2θ ≈ 23.12, 38.24, 45.15, 48.29, 55.11, 64.14, 65.47 which corresponds to (2 2 1), (0 0 4), (3 2 3), (1 4 3), (4 4 0), (541) and (6 2 2) planes of Mn_2O_3 respectively. All of the diffraction peaks of Mn_2O_3 were indexed as body center cubic structure with space group of Ia-3 (206), which is in good accordance with the standard joint committee powder diffraction system (JCPDS), Card No. 41-1442 [3]. Similarly, Co_3O_4 nanoparticles exhibited a strong diffraction peak at 2θ ≈ 36.85 for the plane (3 1 1) and series of peaks at 2θ ≈ 19.00, 31.27, 38.27, 44.81, 55.65, 59.35, 65.27 are corresponding to (1 1 1), (2 2 0), (2 2 2), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) planes respectively. All the observed diffraction peaks are well matched with standard JCPDS, card No. 42-1467 which indicates that the synthesized Co_3O_4 naoparticles have face center cubic structure with space group of Fd-3m (227) [4]. In addition, the lattice parameter and unit cell volume of Mn_2O_3 and Co_3O_4 nano particles were calculated and presented in table 1. Fig. 2. (a) & (b) shows the visualization images of crystal structure of Mn_2O_3 and Co_3O_4 nano particles. Mn_2O_3 showed body centered cubic unit cell with 16 formula units per unit cell cross-linking of double or triple chains of the [MnO6] octahedral. Co_3O_4 showed octahedral and tetrahedral side oxygen bond with cobalt atoms.

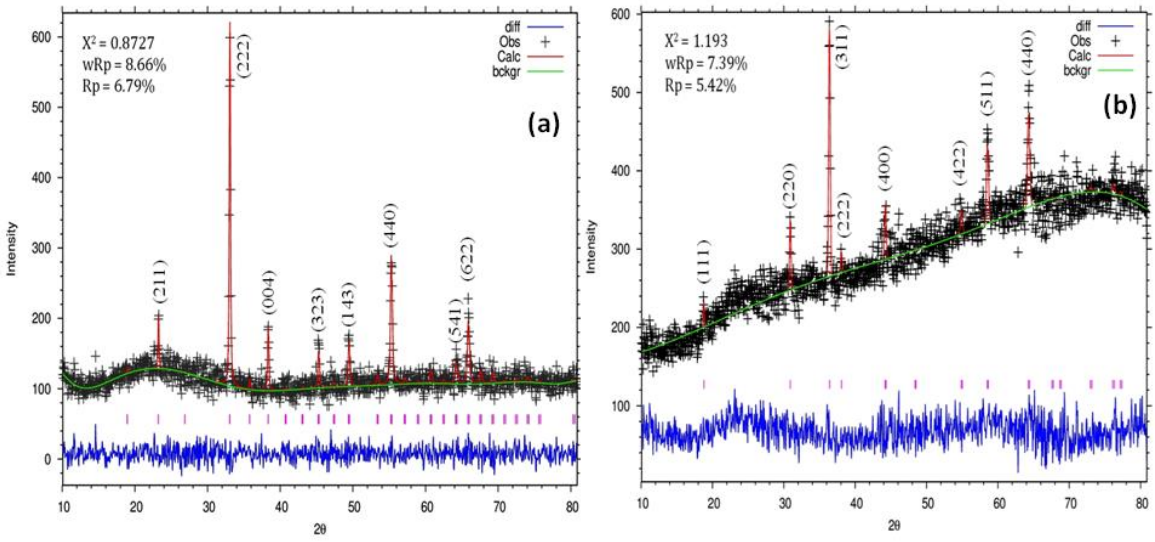

Figure 1. (a) & (b) X-ray diffraction patterns of Mn_2O_3 and Co_3O_4 nanoparticles

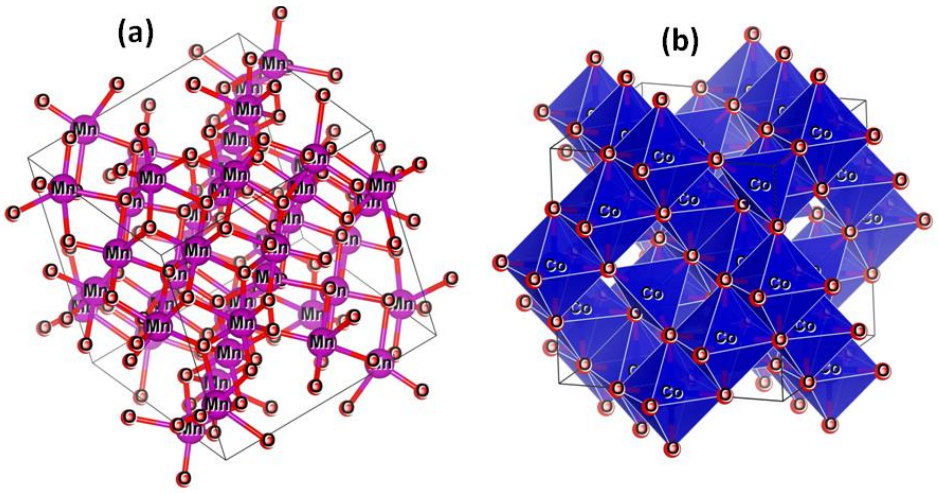

Figure 2 (a) & (b) Crystal structure Visualization view of Mn_2O_3 and Co_3O_4

Table 1. Lattice parameter and cell volume of Mn_2O_3 and Co_3O_4 nano particles

Materials	*a (Å)*	*b (Å)*	*c (Å)*	*Cell volume(Å^3)*
Mn_2O_3	9.4122	9.4122	9.4122	833.829
Co_3O_4	8.1998	8.1998	8.1998	551.341

Fig.3 shows the FTIR spectra of resulting Mn_2O_3 and Co_3O_4 nanonparticles. The weak bands exhibited at around 3452 and 1638 cm^{-1} are corresponding to O-H stretching and bending vibrations modes. In addition, the Mn_2O_3 shows two strong characteristic bands at 523 and 575 cm^{-1} which are attributed to Mn-O stretching vibration modes [5] and Co_3O_4 nanoparticles showed significantly strong and sharp peaks at 556 and 647 cm^{-1}. The absorption band at around 556 cm^{-1} was assigned to Co-O stretching vibration mode and 647 cm^{-1} was assigned to the bridging vibration of O-Co-O band [4].

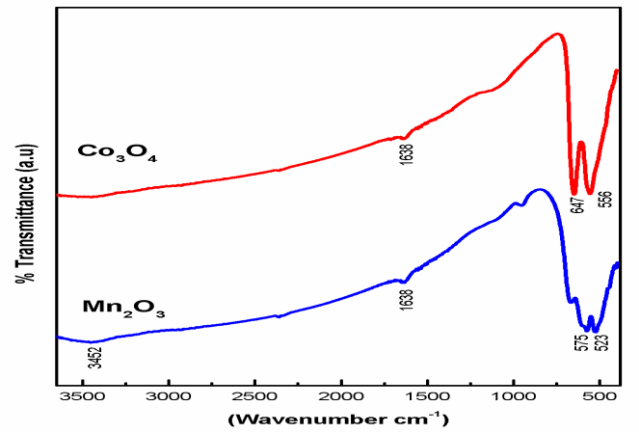

Fig. 3 FTIR spectra of Mn_2O_3 and Co_3O_4 nanoparticles.

Fig. 4 (a) & (b) shows the Raman spectra of the prepared Mn_2O_3 and Co_3O_4 nanoparticles. The Raman bands at around 200 –1000 cm^{-1} arose from the Mn-O and Co-O vibration modes of manganese oxides and cobalt oxides. Three Raman bands are centered at 368, 483 and 652 cm^{-1}.The main characteristic peak observed at 652 cm^{-1} of Mn_2O_3 corresponding to Mn(III)-O mode of vibration [5] and Co_3O_4 shows four Raman bands appeared at 370, 438, 495 and 670 cm^{-1}. Raman mode at 670 cm^{-1} is attributed to the characteristic of the octahedral site and other modes are likely related to the combined vibration of tetrahedral and octahedral sites of oxygen motions of Co_3O_4 nano particles [9].

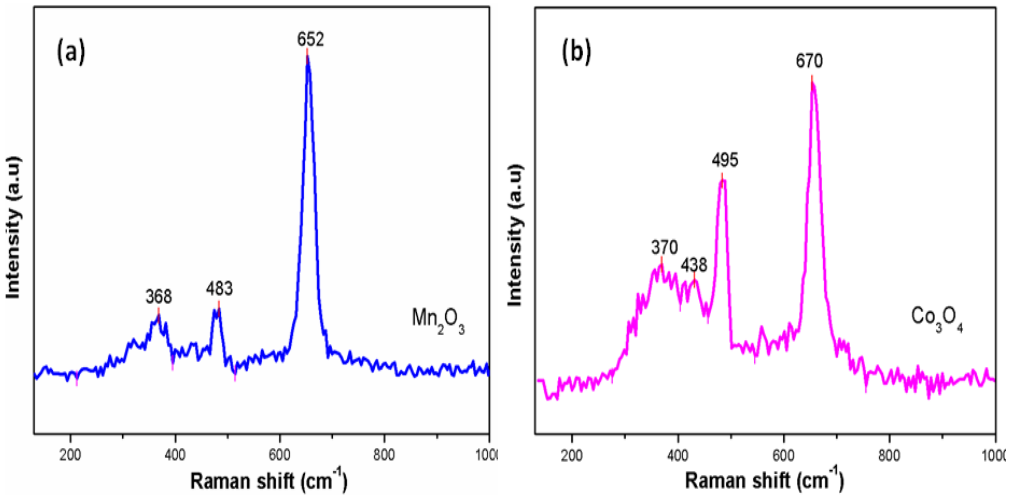

Figure 4 (a) & (b) Raman spectra of Mn_2O_3 and Co_3O_4 nanoparticles

Figure 5 shows the Photoluminescence (PL) spectra of the prepared Mn_2O_3 and Co_3O_4 nano particles. The PL spectra of Mn_2O_3 and Co_3O_4 were recorded at room temperature using a Xenon excitation source with an excitation wavelength of 375 and 360 nm. The spectra exhibit prominent emission bands located in green–violet spectral region. Mn_2O_3 showed three signal peaks were located at 406, 484 and 512 nm and similarly three signal peaks were appeared at 415, 488 and 505 nm for Co_3O_4. The Mn_2O_3 and Co_3O_4 nanoparticles exhibited strong blue emission bands at 484 and 488 nm and an extra weak green peak at 512 and 505 nm. The blue emission at 484 and 488 nm may be assigned to the oxygen vacancy-related defects and an additional broad and weak green emissions at 512 and 505 nm can be attributed to surface dangling bonds or surface defects [3-4].

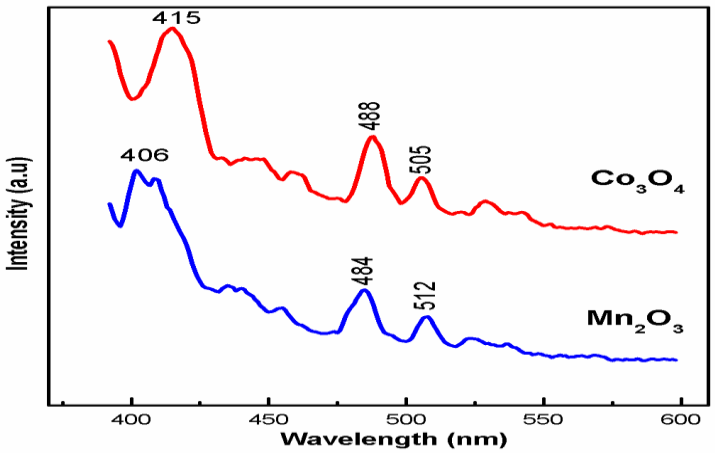

Figure 5. Photoluminescence (PL) spectra of Mn_2O_3 and Co_3O_4 nanoparticles

The magnetic measurements were carried out for Mn_2O_3 and Co_3O_4 samples by using vibrating sample magnetometer (VSM) at room temperature (300 K) in the magnetic field (H) range $-15 \leq H \geq 15$ KOe, respectively and are shown in figures 6(a) and 6(b). The VSM data of Co_3O_4 nano particles show weak ferromagnetic behavior with saturation magnetization (M_s) of about 2.4036 emu/g for the applied maximum magnetic filed (H) of 15 KOe. It is observed from the literature that bulk Co_3O_4 materials normally exhibited an antiferromagnetic behaviour. The change of magnetic behaviour is depends on size and shape of the materials [6]. Mn_2O_3 sample show antiferromagnetic behavior with saturation magnetism (M_s) of about 1.7563 emu/g for that applied magnetic field (H) of 10 KOe. This contradictions result may be due to the synthesis method of Mn_2O_3 [7,8]. The calculated values of coercivity (H_c), retentivity (M_r) and squareness ratio for Mn_2O_3 and Co_3O_4 nanoparticles are listed in table 2.

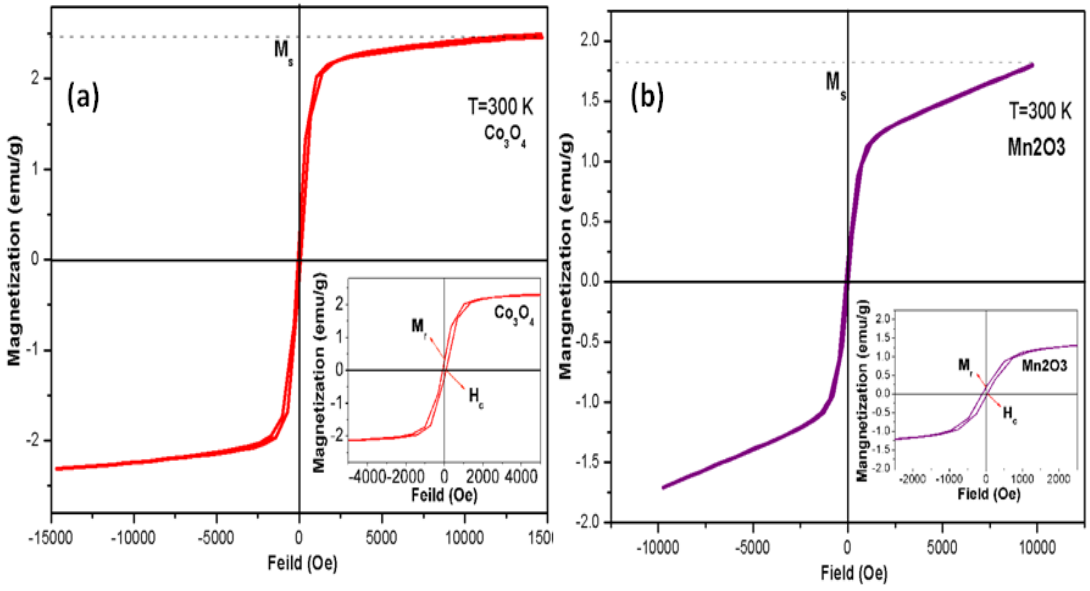

Figure 6 (a) & (b) Vibrating sample magnetometer (VSM) studies on Co_3O_4 and Mn_2O_3 nanoparticles

Table 2. Calculated magnetic parameter values for Co_3O_4 and Mn_2O_3 nanoparticles

Materials	*M_s (emu/g)*	*M_r (emu/g)*	*H_c (Oe)*	*SQR*
Co_3O_4	2.4036	0.24835	87.163	103.3241×10^{-3}
Mn_2O_3	1.7563	0.18469	68.111	105.1585×10^{-3}

IV. CONCLUSION

Mn_2O_3 and Co_3O_4 nanoparticles were synthesized by facile microwave assisted method. XRD patterns were fitted with Rietveld refinement method which reveals that Mn_2O_3 has body centered cubic structure and Co_3O_4 exhibit face centered cubic structure. The FTIR spectra showed the presence of Mn-O and Co-O stretching vibrations. The Raman spectra confirmed the formation of Mn_2O_3 and Co_3O_4 phases. The PL spectra of Mn_2O_3 and Co_3O_4 exhibited strong blue emission band at 484 and 488 nm and a weak defect-related green emission bands at 512 and 505 nm. From magnetic study, Co_3O_4 nano particles demonstrated weak ferromagnetism and Mn_2O_3 reveals antiferromagnetism. It is concluded these results, both materials are more suitable for data storage and magnetic applications.

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