STRUCTURAL AND PHASE ANALYSIS OF PURE AND METAL ION DOPED Mn_2O_3 NANOPARTICLES PREPARED BY MICROWAVE ASSISTED SOL-GEL METHOD

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ABSTRACT

The Fe doped Mn_2O_3 nanoparticles were synthesized by the microwave-assisted method and synthesized samples were further annealed at 500°C and the samples were subjected to analyze structural, optical and magnetic properties. The structural properties of the nanoparticles were characterized by using X-ray diffractometry. XRD pattern revealed that the existence of Mn_2O_3 with cubic structure and Mn-doped Fe is a rhombohedral lattice structure. FTIR spectroscopy confirmed the formation of Fe-O stretching vibrations. The observed band positioned at 570 cm^{-1} could be due to the stretching vibration of Fe-O bonds. Energy dispersive analysis (EDAX) spectroscopy confirmed the purity, chemical composition of the FeMn_2O_3 nanoparticles. The structural properties were analyzed by scanning electron microscope (SEM) analysis.

Keywords: Mn_2O_3 , Nanoparticle, XRD, SEM, EDAX.

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INTRODUCTION

Manganese oxide powder has a wide variety of applications it is used as electrode material¹ catalysts for removing carbon monoxide and nitrogen oxides from air² and also used for preparations soft magnetic material³. Nanometric-sized manganese oxides with remarkably increased surface area and greatly reduced size are expected to display better performance in these aspects of application⁴ and therefore it is prepared by many methods such as solid-state synthesis technique,⁵ thermal conversion route,⁶ chemical precipitation,⁷ solvothermal and hydrothermal methods⁸. Co-precipitation technique⁹ ultrasonication¹⁰ and microwave radiation.¹¹⁻¹² However the ceramic synthesis for various applications¹³⁻¹⁵ nowadays, several reports explain the microwave synthesis route.¹⁶ There are a lot of advantages of the microwave radiation method some of them are heating speed is high, particular system heating is possible, heating takes place by microwaves and there is no need of substantial contact among the vessel and surface material¹⁷⁻¹⁹. The structural arrangements of cations in the bixbyite and orthorhombic bixbyite and their applications were already reported.²⁰ The present work reports how to change the structural properties in different concentrations of Mn and Fe $\text{Fe}_x\text{Mn}_{2-x}\text{O}_3$ the synthesis of Fe doped Mn_2O_3 nanoparticles using MnCl_2 , FeCl_2 and NaOH precursors employing microwave-assisted route.

EXPERIMENTAL

In the present study, $\text{Fe}_x\text{Mn}_{2-x}\text{O}_3$ nanoparticles were prepared from the aqueous solution of MnCl_2 and FeCl_2 . The obtained solutions were reduced by NaOH. Mn_2O_3 nanopowder (FeMnO-1) was prepared from the aqueous solution of MnCl_2 (1M) reduced by NaOH (1M). In this process, 1molar (1M) MnCl_2 powder was added to 100ml distilled water in a roundbottom flask and then the NaOH (1M) was slowly added into the above solution dropwise resulted in solution was kept under constant stirring for an hour to form

a brown color solution. The solution thus obtained was heated in a domestic microwave oven (540 W, 92° C) for 20 minutes. After microwave processing, the mixture was cooled to room temperature and the resulted brown precipitate was separated by centrifugation followed by repeated washing with distilled water and absolute ethanol to remove the impurities and residual materials. After washing, the nanoparticles were dried at 60° C. Finally the prepared materials were annealed at 500°C for three hours. The same procedure of Mn_2O_3 with adding FeCl_2 to dope with Fe in various proportions as it table to synthesis Fe doped Mn_2O_3 . The prepared sample details are listed in Table-1.

Table-1: Prepared Sample Details

Sample Id	Molar Volume of MnCl_2	Molar Volume of FeCl_2
FeMnO-1	1 M	-
FeMnO-2	0.80 M	0.20 M
FeMnO-3	0.60 M	0.40 M
FeMnO-4	0.40 M	0.60 M
FeMnO-5	0.20 M	0.80 M
FeMnO-6	-	1 M

Structural analysis of the prepared samples was analyzed from the recorded XRD spectra using the PANalytical X-pert pro-X-ray diffractometer, the metal-oxide phase formation was confirmed by using the FTIR spectra recorded in the Bruker spectrometer. All the synthesized pure and doped samples were analyzed by VARIAN CARY 5000 scanning electron microscope fitted with EDAX. The surface morphology of the prepared samples were recorded using the JOEL model JSM -690LV instrument (SEM).

RESULTS AND DISCUSSION

Structural Analysis

X-ray diffraction is a very important tool used for extracting information regarding microstructure such as space group, lattice type, unit cell, unitcell volume, structural imperfections and crystalline size etc. The crystalline size and lattice parameter are a very important factor which would be extracted from the XRD peak width analysis. In Fig.-1 the Mn_2O_3 (FeMnO-1) sample without Fe doping with $x=0$ and the peak positions corresponds to Mn_2O_3 . The prepared sample is thus in single-phase without any additional phases like MnO and or Mn_3O_4 . The peak positions observed at specified 2θ values are compared with the JCPDS standards (JCPDS card no:01-089-0436). The lattice type is cubic and hence the structural and defect parameters were calculated accordingly and listed in Table-1. As observed the unit cell parameters, unit cell volume and density are almost equal to the standard values. The calculated crystallite size is 38nm and the strain value is 0.78×10^{-3} .

Fig.-1: XRD Pattern of $\text{Fe}_x\text{Mn}_{2-x}\text{O}_3$ prepared with $x=0$

The role of dopant in individual nanostructures becomes more significant in the doped sample FeMnO-2 with $x=0.2$ ($\text{Fe}_{0.2}\text{Mn}_{0.8}\text{O}_3$). Fig.2 (a) shows the XRD pattern of FeMnO-2 sample which is a composite consisting of Mn_2O_3 and Fe_2O_3 phase (JCPDS Standards 00-013-0534 and 00-041-1442). The Mn_2O_3

phase is cubic and the Fe_2O_3 phase is in the rhombohedral lattice. Calculated unit cell parameters and other related structural parameters are listed in Table-1 for both the phase the unit cell of cubic Mn_2O_3 is almost equal and the rhombohedral parameters $a=4.96 \text{ \AA}$ and $c=13.825 \text{ \AA}$ are comparable with the standard $a=5.031 \text{ \AA}$ and $c=13.737 \text{ \AA}$. Other related structural parameters like unit cell volume and density also are calculated respectively for both the phase. The crystallite size and microstrain values are almost the same for the two phases. By increasing the dopant concentration of Fe ($x=0.4, 0.6$ and 0.8) the obtained nanoparticles are in FeMnO_3 phase with rhombohedral structure (JCPDS Card No: 00-013-0534).

Fig.-2: X-ray Diffraction Patterns of $\alpha\text{-FeMn}_2\text{O}_3$ Sample prepared using NaOH Solutions of different Concentration (a), $x=0.2$, (b), $x=0.4$, $x=0.6$, $x=0.8$. (c) $x=1$

Table-2: Structural Parameters of Pure and Fe Doped Mn_2O_3 Nanoparticles

Sample Details	Lattice Parameter ($\text{\AA}$)		Volume ($\text{\AA}^3$)		Density (g/cm^3)		Crystalline Size (nm)	Strain $\times 10^{-3}$
	Exp	Std	Exp	Std	Exp	Std		
FeMnO-1	$a=9.33$	$a=9.406$	828.243	832.18	5.06	5.04	38.27	0.7810
FeMnO-2 ₁	$a=9.396$	$a=9.409$	818.58	833	5.12	5.03	38.28	0.675
FeMnO-2 ₂	$a=4.96$ $c=13.825$	$a=5.031$ $c=13.737$	294.67	301.11	5.39	5.27	39.88	0.239
FeMnO-3	$a=5.026$ $c=13.689$	$a=5.031$ $c=13.737$	299.54	301.11	5.30	5.27	45.93	0.847
FeMnO-4	$a=5.022$ $c=13.707$	$a=5.031$ $c=13.737$	299.50	301.11	5.31	5.27	60.72	0.634

FeMnO-5	a=5.027 c=13.697	a=5.031 c=13.737	299.81	301.11	5.30	5.27	47.18	0.821
FeMnO-6	a=5.011 c=13.674	a=5.028 c=13.730	297.47	300.60	5.34	5.26	38.13	1.11

Prominent peaks of the resulted samples correspond reflections (012), (104), (110), (024), (116) planes are in perfect 2θ locations as that of the standard data the XRD parameters of the samples are shown in Fig.-2 (b) and the parameters of the calculated structure are listed in Table-1. In all the samples the lattice parameter, unit cell volume and density values are comparable with the JCPDS values. However, the crystalline size increases with the Fe dopant (x). In FeMnO-6 (Fe_2O_3) is rhombohedral structure (JCPDS 00-001-1053) ($a=b$ $a=5.028$ & $c=13.700$) and the values of crystallite size and microstrain are displayed in Table-2. When x is fixed at 1.0 M (FeCl_2) the resulted sample is Fe_2O_3 . The lattice parameters of all the samples were estimated from the William-Hall plot. It was found that the dopant concentration has a profound influence in forming lattice type, lattice constant and defect parameter.

Identification Phase Formation Using FTIR

FTIR spectrum of Fe doped Mn_2O_3 nanoparticles is given in (Fig.-3) FTIR spectrum of $\text{Fe}_x\text{Mn}_{2-x}\text{O}_3$ nanoparticles was studied between 400 cm^{-1} to 4000 cm^{-1} . The strong band below 700 cm^{-1} is assigned Fe-O stretching mode. The band corresponding to Fe-O stretching mode of Fe_2O_3 is seen at 570 cm^{-1} . The peaks at 1695.4 to 1699 cm^{-1} can be related to stretching and bending vibrations of the OH group of water.²¹ FeMnO-1 sample is the pure Mn_2O_3 sample without the dopant Fe ions. Hence the observed broadband in the wavenumber region 527 and 671 cm^{-1} corresponds to the stretching vibrations of Mn-O and Mn-O-Mn bonds of the Mn_2O_3 sample.²²⁻²⁴ Similarly the broad centered around 945.2 cm^{-1} is clear evidence for the formation of Mn_2O_3 corresponds to O-H bending vibrations.²⁵ Since FeMnO-2 is a composite consisting of both Mn_2O_3 and Fe_2O_3 observed broadband in the lower wavelength region and the peak at 944.6 cm^{-1} confirmed the presence of Mn_2O_3 phase.

Fig.-3: FTIR Spectra of $\text{Fe}_x\text{Mn}_{2-x}\text{O}_3$ Samples prepared for Different x Values

However, the presence of Fe_2O_3 phase modifies the broadband in its rising edge. Since 570 cm^{-1} corresponds to the Fe-O stretching vibrations; modification is visible in the spectrum. Hence through the FTIR spectrum also one can confirm the composite nature of the sample as that of XRD. The other phase samples FeMnO-3, FeMnO-4 and FeMnO-5 are in FeMnO_3 phase, but the Fe content is gradually increased, whereas Mn content is reduced. Since the stretching vibration of Fe-O bond is very sharp at almost 570 cm^{-1} .²⁶ The strength of this bond gradually improved on increasing the Fe content. Comparatively the low wavenumber band at almost 470 cm^{-1} that corresponds to the Mn-O stretching is degraded as Fe content increases. In FeMnO-6 sample, Mn content is zero and so the product is Fe_2O_3 and so the peak at 570 cm^{-1} is very strong indicating the presence of Fe_2O_3 only. Since nanoparticles are more

reactive, its surface is susceptible to the water of hydration. This can be confirmed through the bands observed at almost 1700cm^{-1} . That corresponds to the asymmetric stretching of H_2O molecules similarly, observed band at 2350cm^{-1} corresponds to the region O-C-O vibrations. Hence FTIR spectra reveal the formation of $\text{Fe}_x\text{Mn}_{2-x}\text{O}_2$.

Surface Morphology of $\text{Fe}_x\text{Mn}_{2-x}\text{O}_3$ Samples

Figure-4 (a) to (f) are the recorded micro images of the prepared $\text{Fe}_x\text{Mn}_{2-x}\text{O}_3$ with $x=0$. With different x values.

Fig.-4: SEM Images of $\text{Fe}_x\text{Mn}_{2-x}\text{O}_3$ samples with $x=0$, $x=0.2$, $x=0.4$, $x=0.6$, $x=0.8$ and $x=1$

There is no specific change in the SEM analysis of the samples upon doping with Fe. However, the doping level x increases the crystals are looking similitude more porous and same as observed increase in volume in Table-3.²⁷ The Fe doped Mn_2O_3 nano clusters are un uniformly spread compared to undoped Mn_2O_3 nanoparticles. The Fe doped Mn_2O_3 nanoparticles are spherical. Pure Mn_2O_3 samples exhibit distinct particles of non-spherical morphology. However, each particle is distinct with specific edges from which the average particle size was estimated as almost 534 nm. On doping Fe with $x=0.2$, obtained particles well dispersed and the particle size is reduced the average particle size is about 350nm. Since the prepared sample is a composite having Fe_2O_3 and Mn_2O_3 phase the particle growth is not obtained. However, an increasing concentration of Fe prepared material is a single phase with FeMnO_3 the particle is visible. The obtained particle sizes are respectively 547, 566, and 571 nm for the dopant concentrations $x=0.4$, 0.6 and 0.8. In the sample $\text{Fe}_x\text{Mn}_{2-x}\text{O}_3$ with $x=1$, all the Mn atoms are replaced by Fe atoms and hence the entire morphology is completely different. All the particles are spherical and are of equal size 424 nm. Hence the physical impregnation of Fe ions counts Mn_2O_3 lattice is visible through SEM studies.

Elemental Analysis (EDAX)

The interaction of an electron beam with the sample target produces a variety of emission X-ray peaks correspond to the elements present in the sample. From the recorded peak positions formation of the compound can be confirmed. The EDAX spectra of pure Mn_2O_3 and Fe doped Mn_2O_3 samples are shown in Fig.-4 The EDAX spectra shows the peaks corresponding to manganese, oxygen and manganese, oxygen, ferric elements interfering that the prepared samples contain only Mn, O and Mn, Fe and O elements respectively. The result confirms the purity of grown nanomaterial with no additive impurities. The mixed nano compositions of elements weight percentage in each sample are given in Table-4. In Fig.-4(a), this corresponds to the Mn_2O_3 sample that shows peaks corresponding to manganese and oxygen alone. Other samples Fe doped samples and hence additional peaks corresponding to the elements Fe also is seen. Since the spectra Fig.-4(f) is for the Fe_2O_3 samples only Fe and O elements are detectable. Since the doping concentration varies from $x=0$ to 1 in steps of 0.4, the concentrations of elements also vary accordingly. These variations both in atomic and mass percentages are shown Table-3.

Table-3: Elements in Atomic and Mass Percentage of $\text{Fe}_x\text{Mn}_{2-x}\text{O}_3$ Sample

Sample, $\text{Fe}_x\text{Mn}_{2-x}\text{O}_3$	Elements	From EDAX	
		Wt %	Atom %
$x=0$	Mn	31.24	60.95
	O	67.89	38.57
	Fe	0.86	0.48
$x=0.2$	Mn	23.89	14.27
	O	28.0	57.45
	Fe	48.11	28.28
$x=0.4$	Mn	9.01	5.76
	O	21.87	48.07
	Fe	64.93	40.89
$x=0.6$	Mn	5.06	2.93
	O	25.89	51.43
	Fe	57.76	32.87
$x=0.8$	Mn	2.79	1.65
	O	27.41	55.68
	Fe	66.35	38.62
$x=1$	Mn	0	0
	O	32.32	62.13
	Fe	65.84	36.26

Fig.-5: EDAX Spectra of $\text{Fe}_x\text{Mn}_{2-x}\text{O}_3$ Sample prepared with $x=0, x=0.2, x=0.4, x=0.6, x=0.8$ and $x=1$

CONCLUSION

Fe doped Mn_2O_3 nanoparticles were prepared by Microwave-assisted technique by various concentrations. The effects of the structural and morphology of the prepared nanoparticles were investigated. XRD study revealed the rhombohedral structure and their crystallite sizes were gradually improved on increasing substrate concentrations. FTIR spectra confirmed the metal oxide phase formation with Mn-O stretching band. SEM analysis revealed smooth and crack-free surfaces and the surface microstructure has a dependence on substrate concentrations. EDAX spectra confirmed the structure of Pure and Fe doped Mn_2O_3 nanoparticles.

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