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STUDY OF STRUCTURAL, AND ANTIBACTERIAL PROPERTIES OF Fe_xMn_(1-x)O₃NANOPARTICLES PREPARED BY MICROWAVE ASSISTED PRECIPITATION TECHNIQUE

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Abstract

The Fe doped Mn₂O₃ nanoparticles were synthesized by the microwave-assisted method and synthesized sampleswere further annealed at 500°C and the samples were subjected to analyze structural and Phase Analysisproperties. The structural properties of the nanoparticles were characterized by using X-ray diffractometry. XRDpattern revealed that the existence of Mn₂O₃ with cubic structure and Mndoped Fe is a rhombohedral latticestructure. The Raman analysis confirms the phase formation of the prepared samples.

1. INTRODUCTION

Fe₂O₃ nano materials have a wide variety of applicationsamong the metal oxides based systems. It is most widely studied materials in recent literature due to their impressive properties and magnetic strength and its ability to utilize technologies such as in biotechnology, electrochemistry, catalysis, magnetism and biomedicine. [1-3],in meticulous Fe₂O₃ nanoparticles have concerned momentous concentration for prospective applications in electronics [4] fuel cells [5]. Manganese oxide is non stoichiometry composite when it is doped by ferric ion. In the Fe doped manganese oxide has various applications including magnetic property, dielectric, catalytic, dissolution, electrochemical and electromagnetic absorbance. Manganese oxide is an ideal oxidizing agent it is used to remove the toxic contaminants from the drinking water [6]. In the nanoparticles research, size dependent is an important property. It plays a main roll in tailoring properties [7]. Fe doped manganese oxide nanoparticles considered to exist mainly typical spinel structure tetrahedral siteswith 80% are occupied by Mn²⁺ ions [8]. It is also having insulating properties with a very small gap [9]. Warner et al. investigated Mn-doped Fe₃O₄ nanoparticles use of heavy metal origin as of aqueous solutions [10]. Recent years in particular renewed attention in hematiteα-Fe₂O₃ nanoparticles [11-13]. Hence in this chapter the preparation of Fe doped Mn₂O₃ nanoparticles and its structural, optical and morphological properties were discussed.

2.EXPERIMENTAL PROCEDURE

Among the available methods simple microwave assisted synthesismethod has been chosen because this method is less expensive and an efficient technique for the preparation of transition metal oxides. In this method heat can be transferred easily to the solution and the heating temperature can be selected precisely.

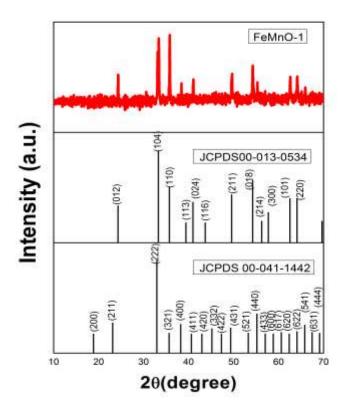
In the present study Fe_xMn_(1-x)O₃ nano powder were prepared from the aqueous solution of MnCl₂ and FeCl₂.FeMnO-1nano powder were prepared from the aqueous solution of FeCl₂ (0.2 M), MnCl₂ (0.8 M) reduced by NaOH(1M). In this process, required amount FeCl₂and MnCl₂ powder were added to 100ml distilled water in a roundbottom flask and then the NaOH pellets were slowly added in to the above solution resulted solution was kept under constant stirring for an hour to from a brown colour 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 nano particles were dried at 60 °C. Finally, the prepared materials wereannealed at 500°C for three hours. The same procedure is repeated to dope with Fe in various proportions FeMnO-2(MnCl₂ 0.60and FeCl₂ 0.40), FeMnO-3(MnCl₂ 0.40and FeCl₂ 0.60), FeMnO-4 (MnCl₂ 0.20and FeCl₂ 0.80) and FeMnO-5 (FeCl₂ 1M). Thus Fe_xMn_(1-x)O₃ powder was prepared for $\kappa = 0.2, 0.4, 0.6, 0.8$ and 1M. Prepared samples were named as FeMnO-1, FeMnO-2 FeMnO-3 FeMnO-4 and FeMnO-5.

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3.RESULT AND DISCUSSION

3.1 Structural Analysis

X-Ray diffraction is very important tool used for extracting information recording microstructure like space group, lattice type, unit cell, unitcell volume, structural imperfections, crystalline size etc. The crystalline size and lattice parameter are very important factor which would be extracted from the XRD



peak width analysis.

Fig.1 X-ray diffraction pattern of $Fe_{\varkappa}Mn_{(1-\varkappa)}O_3$ sample prepared with $\varkappa=0.2$

The role of dopant in individual nanostructures becomes more significant in the doped sample FeMnO-1 with $\varkappa=0.2$ (Fe_{0.2} Mn_{0.8}O₃). Fig.1 shows the XRD pattern of FeMnO-1 sample. It reveal that the sample is a composite consisting of Mn₂O₃ and Fe₂O₃phase. This could understand on matching the peaks for the JCPDS Standards 00-013-0534 and 00-041-1442. The Mn₂O₃ phase is cubic and the Fe₂O₃ phase is in rhombohedral lattice. Calculated unit cellparameters and other related structural parameters are listed in Table 1.

The unit cell edges of both cubic Mn₂O₃ (a=9.396 Å) and rhombohedral Fe₂O₃ (a=4.96 Åand c=13.825Å) arealmost equal and they are comparable with the standard JCPDS values (a=9.409 Å),(a=5.031Åand c=13.737Å).Other related structural parameters like unit cell volume and density are calculated respectively for both phase. The crystallite size and micro strains values are almost the same for the two phases.

Fig 2 shows the XRD pattern of $Fe_{\varkappa}Mn_{(1-\varkappa)}O_3$ sample prepared with $\varkappa=0.4$, 0.6 and 0.8. From the obtained results it is revealed that the prominent peaks corresponds reflections (012), (104), (110), (024), (113), (116) (018), (214) and (300) planes are in perfect 20 locations of rhombohedral phase of FeMnO3as that of the standard JCPDS data [JCPDS Card No: 00-013-0534]. Moreover the

FeMnO₃ phase with rhombohedral structure belongs to the space group=R-3c and space group number=167. The structural parameter of all the samples were calculated and listed in the Table 1.

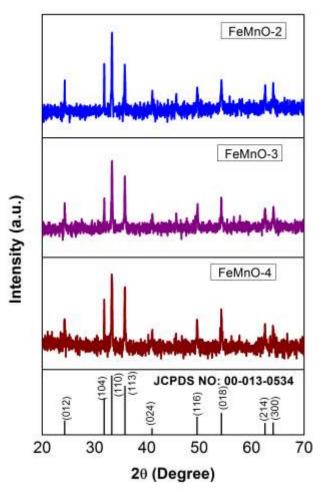


Fig.2XRD patterns of $Fe_{\varkappa}Mn_{(1-\varkappa)}O_3$ sample prepared with $\varkappa=0.4, 0.6$ and 0.8

In all the samples the lattice parameter values are almost the same and are comparable with the JCPDS values. So the unitcell volume and the density are almost the same. However, the crystalline size increase initially with \varkappa values and the decreases the variation of microstrain follows similarly.

In the sample FeMnO-5, \varkappa value is fixed at 1 mole (1M) and the peak appearing at 2 θ range of 33.28°, 35.74°, 49.49°, 54.23°, 62.26° and 64.17° can be attributed to the plane (104), (110), (024), (116), (214) and (300) respectively. The crystalline structures of the corresponding sample is Hematite iron oxide nanoparticlesin Rhombohedral structure (a=b a=5.0280, c=13.700) space groupR-3c and space group number 167. The peaks are perfectly matched using Cell Cal software and are found in match with the standard values (00-001-1053). The Mn and Fe have several oxidation states. The ionic radius of Fe²⁺ ions is 0.78 Å and Fe³⁺ ions is 0.645Å. At the same time Mn ions have smaller ionic radius (Mn²⁺-0.58 Å, Mn³⁺-0.66 Å and Mn⁴⁺-0.53 Å) than the Fe ions [14-15]. The lattice parameter and the crystal size of the Fe doped nanoparticles are higher than that of pure Mn₂O₃ nanoparticles. This result confirmed the expansion of lattice parameter due to the doping of Fe ions in to the Mn lattice. The Mn ions ionic radius is smaller than Fe²⁺ ions. The Fe²⁺ ions might be dominant as the assimilation of material among upper ionic radius will enlarge the lattice, thus raising the particle size [16]. No specific progression in lattice parameter is observed in the Fe doped nanoparticles by the raise in Fe doping. This might be due to the existence of several oxidation states in Mn and Fe; this controls the lattice reduction and lattice expansion of the samples. The unit cell volume is the dependent parameter to lattice constant and so its variation is similar to that of lattice constant. Obtained density values are high than that of the bulk value. The decrease of elastic strain is observed with an increase in particle size the both (crystallite size and micro strain) are having inverse dependency.

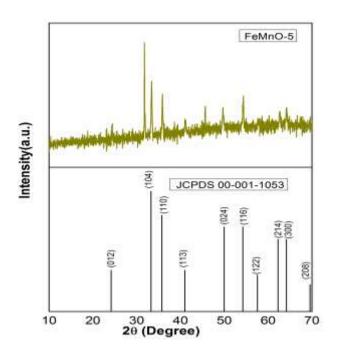


Fig.3X-ray diffraction pattern of FexMn_(1-x)O₃sample with x=1M Table.1Structural parameters of pure and Fe Doped Mn₂O₃ nano particles

Sample Details	LatticeParameter (Å)		Volume (Å) ³		Density (g/cm ³)		Crystalline	Strain x 10
	Exp	Std	Exp	Std	Exp	Std	Size (nm)	3
FeMnO (Cubic)	a=9.396	a=9.409	818.58	833	5.12	5.03	38.28	0.675
FeMnO-1 (rhombohedral)	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-2	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-3	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-4	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-5	a=5.011 c=13.674	a=5.028 c=13.730	297.47	300.60	5.34	5.26	38.13	1.11

3.3 METAL-OXIDE PHASE ANALYSIS USING RAMAN

Raman spectroscopy is the dominant and all-round characterization instrument for determining the semiconductor devices of nano scale and chemical composition analysis of the substance. Raman scattering spectrum was taken in the range from 50-1500 cm⁻¹. The Raman spectra of the prepared samples were displayed in Fig. 4. In the FeMnO-1 sample the observed peaks are placed at 183, 305, 629 and 694 cm⁻¹the first peak 183 cm⁻¹confirms to the presence of manganese oxide [17]. The observedlittle peak at 612 cm⁻¹ corresponds to phonon mode (E_g) and it confirms the presence of Fe ions [18-19]. The another two broad peaks at 305 and 694 cm⁻¹ are in A_{1g} Raman active modes. These two main peaks are principally

accredited the presence of Mn₂O₃ group and symmetric stretch of vibration mode [20-21]. This result confirmed that the sample FeMnO-1 is in mixed phase of both (Fe and Mn). On increase the doping concentration $\varkappa = 0.4$ to 0.8 (FeMnO-2 to FeMnO-4) the observed peaks are shifted to the lower wave number region and the samples arehaving Fe and Mn mixed phase. The FeMnO-5 sample is a pure Fe₂O₃ sample the observed bands 610, 490, 400, 282 and 217 cm⁻¹ are confirm the presence of Fe₂O₃ [22-23]. The A_{1g}modes are assigned to 217 and 490 cm⁻¹ Raman bands and the E_g modes are assigned at 610, 400 and 282 cm⁻¹ band. The main band at around 1310 cm⁻¹ is dispensed to a two-magnon dissipating which emerges from the connection of two magnons made on antiparallel close turn destinations [24-26].

Table.2Previously reported Raman analysis results of Fe₂O₃

Reference	Raman shift (cm ⁻¹)				
Verble et al. [27]	680, 560, 420, 320, 300				
Boucherit et al. [28]	670, 550				
Hart et al. [29]	676, 550, 472, 420, 320, 298				
Dunnwald and Otto. [30]	1322, 676, 550, 470, 418, 319, 298				
Ohtsuka et al. [31]	665, 540				
Thierry et al. [32]	670, 550				
de Faria et al. [33]	662.7, 533.6, 301.6				
Gasparov et al. [34]	670, 540, 308, 193				
Degiorgi et al. [35]	672, 542, 462, 410, 318, 160				
Graves et al. [36]	706, 570, 490, 336, 226				
Romcevic and Kostic. [37]	665, 540, 311				
Gupta et al. [38]	669, 540, 410, 300				
Present study	629, 694, 282, 400, 490, 610, 130				

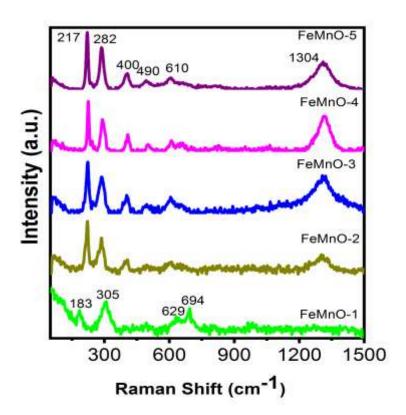


Fig.4. Raman Spectra of FeMn₂O₃ nano particles

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at 723.47 eV. This signifies the presence of Fe³⁺ ions in the prepared Fe₂O₃ sample [39-40]. The iron oxide nanoparticles have very high binding energy value comparable to any other metal oxides [41]. In addition the two weak Fe³⁺shake satellite peaks are observed at 716.73 eV and 731.07 eV. The Fe2p_{3/2} satellite band is appeared around 8 eV this same result have reported by Clara Pereira et al [42]. The spin orbit split value $(2p_{3/2}-2p_{1/2})$ is 14.8 eV. All the experiential results are analogues to XRD results that proved the Fe₂O₃ nanoparticles formation of with no any other impurities.

Conclusion

In summary, smooth and compact FeMn₂O₃ nanoparticles were prepared by microwave assisted synthesis method. The structural variations with various concentrations of the prepared nanoparticles were analyzed. The strong absorption bands are appears around ~ 345 and ~ 530 nm. The absorption spectrum of Fe doped nanoparticles is due to the d-d conversion among higher eg and lowers t2g of the Mn ion

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