STRUCTURAL AND PHASE ANALYSIS OF PURE AND METAL ION DOPED Mn$_2$O$_3$ NANOPARTICLES PREPARED BY MICROWAVE ASSISTED SOL-GEL METHOD

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ABSTRACT

The Fe doped Mn$_2$O$_3$ nanoparticles were synthesized by the microwave-assisted method and synthesized samples were further annealed at 500$^0$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$_2$O$_3$ with cubic structure and Mn-doped Fe isa rhombohedral lattice structure. FTIR spectroscopy confirmed the formation of Fe-O stretching vibrations. The observed band positioned at 570cm$^{-1}$could be due to the stretching vibration of Fe-O bonds. Energy dispersive analysis (EDAX) spectroscopy confirmed the purity, chemical composition of the FeMn$_2$O$_3$ nanoparticles. The structural properties were analyzed by scanning electron microscope (SEM) analysis.

Keywords: Mn$_2$O$_3$, Nanoparticle, XRD, SEM, EDAX.

INTRODUCTION

Manganese oxide powder has a wide variety of applications it is used as electrode material$^1$ catalysts for removing carbon monoxide and nitrogen oxides from air$^2$ and also used for preparations soft magnetic material$^3$. Nanometric-sized manganese oxides with remarkably increased surface area and greatly reduced size are expected to display better performance in these aspects of application$^4$ and therefore it is prepared by many methods such as solid-state synthesis technique,$^5$ thermal conversionroute,$^6$ chemical precipitation,$^7$ solvothermal and hydrothermal methods$^8$. Co-precipitation technique$^9$ ultrasonication$^{10}$ and microwave radiation.$^{11-12}$ However the ceramic synthesis for various applications$^{13-15}$ nowadays, several reports explains 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 material$^{17-18}$. 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 Fe$_{\chi}$Mn$_{2-\chi}$O$_3$ the synthesis of Fe doped Mn$_2$O$_3$ nanoparticles using MnCl$_2$, FeCl$_2$ and NaOH precursors employing microwave-assisted route.

EXPERIMENTAL

In the present study,Fe$_{\chi}$Mn$_{2-\chi}$O$_3$ nanoparticles were prepared from the aqueous solution of MnCl$_2$ and FeCl$_2$. The obtained solutions were reduced by NaOH. Mn$_2$O$_3$ nanopowder (FeMn-O-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

Rasayan J. Chem., 13(4), 2223-2229(2020)
http://dx.doi.org/10.31788/ RJC.2020.1346083
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 Mn₂O₃ with adding FeCl₂ to dope with Fe in various proportions as it table to synthesis Fe doped Mn₂O₃. The prepared sample details are listed in Table-1.

Table-1: Prepared Sample Details

| Sample Id | Molar Volume of MnCl₂ | Molar Volume of FeCl₂ |
|-----------|-----------------------|-----------------------|
| 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, unit cell volume, structure limperfections 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 Mn₂O₃ (FeMnO-1) sample without Fe doping with x=0 and the peak positions corresponds to Mn₂O₃. The prepared sample is thus in single-phase without any additional phases like MnO and or Mn₃O₄. 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 FeₓMn₂−ₓO₃ prepared with x=0

The role of dopant in individual nanostructures becomes more significant in the doped sample FeMnO-2 with x=0.2(Fe₀.2Mn₀.8O₃). Fig.2 (a) shows the XRD pattern of FeMnO-2 sample which is a composite consisting of Mn₂O₃ and Fe₂O₃ phase (JCPDS Standards 00-013-0534 and 00-041-1442). The Mn₂O₃...
phase is cubic and the Fe$_2$O$_3$ 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$_2$O$_3$ is almost equal and the rhombohedral parameters a=4.96 Å and c=13.825 Å are comparable with the standard a=5.031 Å and c=13.737 Å. 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 α-FeMn$_2$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$_2$O$_3$ Nanoparticles

| Sample Details | Lattice Parameter (Å) | Volume (Å$^3$) | Density (g/cm$^3$) | Crystalline Size (nm) | Strain x 10$^{-3}$ |
|----------------|-----------------------|---------------|-------------------|----------------------|-------------------|
| FeMnO-1        | a=9.33                | a=9.406       | Exp               | Exp                  | 38.27             | 0.7810            |
| FeMnO-2        | a=9.396               | a=9.409       | 828.243           | 832.18               | 5.06              | 5.04              | 38.28             | 0.675              |
| FeMnO-2        | a=4.96                | a=5.031       | c=13.825          | c=13.737             | 294.67            | 301.11            | 5.39              | 5.27               | 39.88             | 0.239              |
| FeMnO-3        | a=5.026               | a=5.031       | c=13.689          | c=13.737             | 299.54            | 301.11            | 5.30              | 5.27               | 45.93             | 0.847              |
| FeMnO-4        | a=5.022               | a=5.031       | c=13.707          | c=13.737             | 299.50            | 301.11            | 5.31              | 5.27               | 60.72             | 0.634              |
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 (ϰ). In FeMnO-6 (Fe₂O₃) 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 ϰ is fixed at 1.0 M (FeCl₂) the resulted sample is Fe₂O₃. 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 Mn₂O₃ nanoparticles is given in (Fig.-3) FTIR spectrum of FeₓMn₂₋ₓO₃ 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 Fe₂O₃ 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 Mn₂O₃ 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 Mn₂O₃ sample.²²-²⁴ Similarly the broad centered around 945.2cm⁻¹ is clear evidence for the formation of Mn₂O₃ corresponds to O-H bending vibrations.²⁵ Since FeMnO-2 is a composite consisting of both Mn₂O₃ and Fe₂O₃ observed broadband in the lower wavelength region and the peak at 944.6 cm⁻¹ confirmed the presence of Mn₂O₃ phase.

![Fig.-3: FTIR Spectra of FeₓMn₂₋ₓO₃ Samples prepared for Different ϰ Values](image)

However, the presence of Fe₂O₃ 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 FeMnO₃ 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 470cm⁻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 Fe₂O₃ and so the peak at 570 cm⁻¹ is very strong indicating the presence of Fe₂O₃ 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 1700 cm\textsuperscript{-1}. That corresponds to the asymmetric stretching of H\textsubscript{2}O molecules similarly, observed band at 2350 cm\textsuperscript{-1} corresponds to the region O-C-O vibrations. Hence FTIR spectra reveal the formation of Fe\textsubscript{\(\kappa\)}Mn\textsubscript{2-\(\kappa\)}O\textsubscript{3}.

### Surface Morphology of Fe\textsubscript{\(\kappa\)}Mn\textsubscript{2-\(\kappa\)}O\textsubscript{3} Samples

Figure-4 (a) to (f) are the recorded micro images of the prepared Fe\textsubscript{\(\kappa\)}Mn\textsubscript{2-\(\kappa\)}O\textsubscript{3} with \(\kappa\)=0. With different \(\kappa\) values.

There is no specific change in the SEM analysis of the samples upon doping with Fe. However, the doping level \(\kappa\) increases the crystals are looking similitude more porous and same as observed increase in volume in Table-3.\textsuperscript{37} The Fe doped Mn\textsubscript{2}O\textsubscript{3} nano clusters are un uniformly spread compared to undoped Mn\textsubscript{2}O\textsubscript{3} nanoparticles. The Fe doped Mn\textsubscript{2}O\textsubscript{3} nanoparticles are spherical. Pure Mn\textsubscript{2}O\textsubscript{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 \(\kappa\)=0.2, obtained particles well dispersed and the particle size is reduced the average particle size is about 350 nm. Since the prepared sample is a composite having Fe\textsubscript{2}O\textsubscript{3} and Mn\textsubscript{2}O\textsubscript{3} phase the particle growth is not obtained. However, an increasing concentration of Fe prepared material is a single phase with FeMnO\textsubscript{3} the particle is visible. The obtained particle sizes are respectively 547, 566, and 571 nm for the dopant concentrations \(\kappa\)=0.4, 0.6 and 0.8. In the sample Fe\textsubscript{\(\kappa\)}Mn\textsubscript{2-\(\kappa\)}O\textsubscript{3} with \(\kappa\)=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\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{3} and Fe doped Mn\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{3} samples only Fe and O elements are detectable. Since the doping concentration varies from \(\kappa\)=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 Fe$_{\chi}$Mn$_{2-\chi}$O$_3$ Sample

| Sample, Fe$_{\chi}$Mn$_{2-\chi}$O$_3$ | Elements | From EDAX |
|------------------------------------|----------|-----------|
|                                   | Wt %     | Atom %    |
| $\chi=0$                          | Mn 31.24 | 60.95     |
|                                   | O  67.89 | 38.57     |
|                                   | Fe  0.86 | 0.48      |
| $\chi=0.2$                        | Mn 23.89 | 42.07     |
|                                   | O  28.0  | 57.45     |
|                                   | Fe  48.11| 28.28     |
| $\chi=0.4$                        | Mn 9.01  | 17.11     |
|                                   | O  21.87 | 43.51     |
|                                   | Fe  64.93| 32.38     |
| $\chi=0.6$                        | Mn 5.06  | 9.95      |
|                                   | O  25.89 | 52.43     |
|                                   | Fe  57.67| 37.62     |
| $\chi=0.8$                        | Mn 2.79  | 5.46      |
|                                   | O  27.41 | 54.87     |
|                                   | Fe  66.35| 39.68     |
| $\chi=1$                          | Mn 0.00  | 0.00      |
|                                   | O  32.32 | 62.13     |
|                                   | Fe  65.84| 36.26     |

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

CONCLUSION

Fe doped Mn$_2$O$_3$ 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 and 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$_2$O$_3$ nanoparticles.

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