

Synthesis and Morphological Study of Mn Substituted Magnesium Ferrites Nanostructures via Sol-gel Method

A.V. Mali^{a*},

^a Department of Chemistry, Yashwantrao Chavan College of Science, Karad -415124, India.

Abstract

Nanocrystalline $Mg_{1-x}Mn_xFe_2O_4$ ($1.0 \geq x \geq 0$) ferrites were prepared by sol-gel method. X-ray diffraction (XRD) method was used to confirm the formation of single phasic cubic spinel lattice for all the composition. Surface morphological studies of the samples were carried out by using scanning electron microscope. Infrared spectroscopic studies revealed two main absorption bands in the range $350-700\text{ cm}^{-1}$ arising due to tetrahedral (A) and octahedral (B) stretching vibrations. The detailed results of XRD, and infrared spectroscopy indicating the role of manganese on the structural properties of magnesium ferrites.

Keywords: Ferrites, Synthesis, X-ray diffraction, EDAX.

^{a*} Corresponding author- ankushvmali@gmail.com

1. Introduction

Mixed-metal oxide nanoparticles have been intensively studied in the last decade due to their unusual physical and chemical properties owing to their extremely small size, large specific surface area and number of promising applications. As a result, numerous applications of metal oxides, such as fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, dielectrics, lasers, magnets and catalysts have discussed[1-8].

Recently, considerable effort has been made on the surface modification of nanoparticles and the preparation of different type of metal oxides. Various methods are available for the synthesis of metal oxides, such as microwave refluxing [9], sol-gel [10], hydrothermal [11] co-precipitation [12], citrate-gel [13] and spray pyrolysis [14] etc. The selection of appropriate synthetic procedure often depend on the desired properties and final applications. Among these synthesis techniques, sol-gel autocombustion method has several advantages over others for preparation of nanosized metal oxides as the process begins with a relatively homogeneous mixture and involvement low temperature conditions resulting a uniform ultrafine porous powder [15]. In our previous work [16-17] this method was employed to obtain improved powder characteristics, more homogeneity and narrow particle size distribution, thereby influencing structural, electrical and magnetic properties of spinel ferrites. In this communication, we report preparation of nanosized Mn substituted magnesium ferrites by sol-gel autocombustion method. The structural and morphological properties investigated by X-ray diffraction (XRD), Scanning Electron Microscope analysis and FTIR spectroscopy are discussed in this manuscript.

2 Experimental Techniques

Analytical grade iron nitrate [Fe ((NO₃)₃.9H₂O)], citric acid [C₆H₈O₇.H₂O], manganese nitrate [Mn (NO₃)₂.4H₂O], magnesium nitrate [Mg (NO₃)₂.6H₂O] and ammonia were used to prepare Mg_{1-x}Mn_xFe₂O₄ (where x = 0.0, 0.25, 0.50, 0.75 and 1.0) by sol-gel method experimental detail were reported in our previous paper [18]. The phase formation of the sintered samples were confirmed by x-ray diffraction studies using Ni-filter CuK α radiation. FTIR study was used to indicate the vibrational modes in the samples. The morphology and particle size analysis was carried out on a transmission electron microscope. The composition analysis was performed by an energy dispersive x-ray system (EDAX). The FTIR spectrums were recorded using Perkin Elmer FTIR in KBr pellets.

3 Results and discussion

3.1 X-ray diffraction studies

The powder XRD patterns of the prepared Mg_{1-x}Mn_xFe₂O₄ compositions shown in **Figure 1**. The structure and phase purity of the product were confirmed by analyzing the observed powder X-ray diffraction patterns. All the observed reflections of the manganese substituted magnesium ferrite samples could be assigned to cubic spinel lattice indicating their single phasic nature. The x-ray density (dx), lattice constant (a) and crystallite size (t) are shown in **Table.1**. It is observed that the cubic unit cell parameter of the manganese substituted magnesium ferrite phase gradually increases with increasing Mn content in the composition obeying Vegard's law. The slow linear increasing trend in the lattice parameter is attributed to the replacement of Mg²⁺ (0.65Å) ion by Mn²⁺ (0.80Å). From the X-ray diffraction peaks, average particle size was estimated using Scherrer's formula.

$$t = 0.9\lambda / \beta \cos \theta$$

Where, symbols have their usual meaning. The crystallite size was found to be in the range of 33-42 nm.

The X-ray density (dx) was calculated using the following relation.

$$dx = 8M/Na^3$$

Where, N= Avagadros number (6.023 x 10²³ atom/mole)

M=Molecular weight

a = Lattice constant

The slow increasing trend of unit cell parameter and incorporation of Mn²⁺ in place of Mg²⁺ a gradual increase in the x-ray density with increase in manganese content.

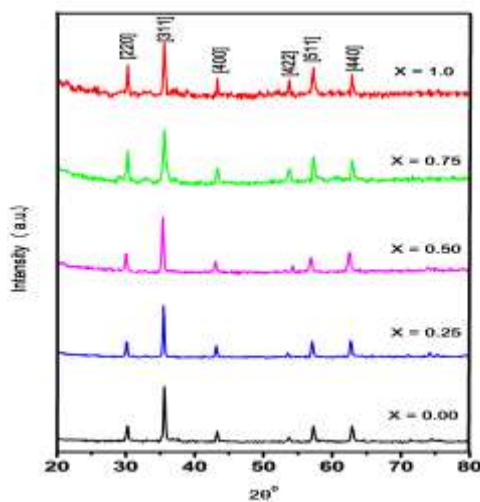


Fig.1. X-ray data for the system $Mg_{1-x}Mn_xFe_2O_4$

Table 1. Lattice constants, Crystallite size and X-ray density for $Mg_{1-x}Mn_xFe_2O_4$ ($0 \leq x \leq 1$).

Sr. No.	Compound	Lattice Constants (Å)	Crystallite Size (nm)	X-ray density (d_x) g/cm ³
1	x = 0.0	8.037	34.41	3.96
2	x = 0.25	8.094	35.46	4.17
3	x = 0.5	8.131	39.62	4.39
4	x = 0.75	8.147	43.93	4.42
5	x = 1.0	8.152	46.14	4.57

3.2 Scanning Electron Microscope analysis

Surface morphological studies of the samples $Mg_{1-x}Mn_xCr_2O_4$ ($x = 0.0, 0.50, 1.0$) sintered at 873K were carried out by using scanning electron microscope (SEM) and they are shown in **Figure.2 (a-c)**. The grain size of the sample was calculated by using Cottrell's method which gives the relation between the number of intercepts of grains boundary per unit length (P_L) and total number of intercepts (n) as

$$P_L = (n / 2\pi r) M$$

Where M is the magnification at which SEM micrograph was scanned, r is the radius of the circle and n is the number of grains in the circle. The larger grain size observed in SEM is due to the significant agglomeration of the crystallites. The SEM micrograph further reveals that the grains are uniformly distributed throughout the surface.

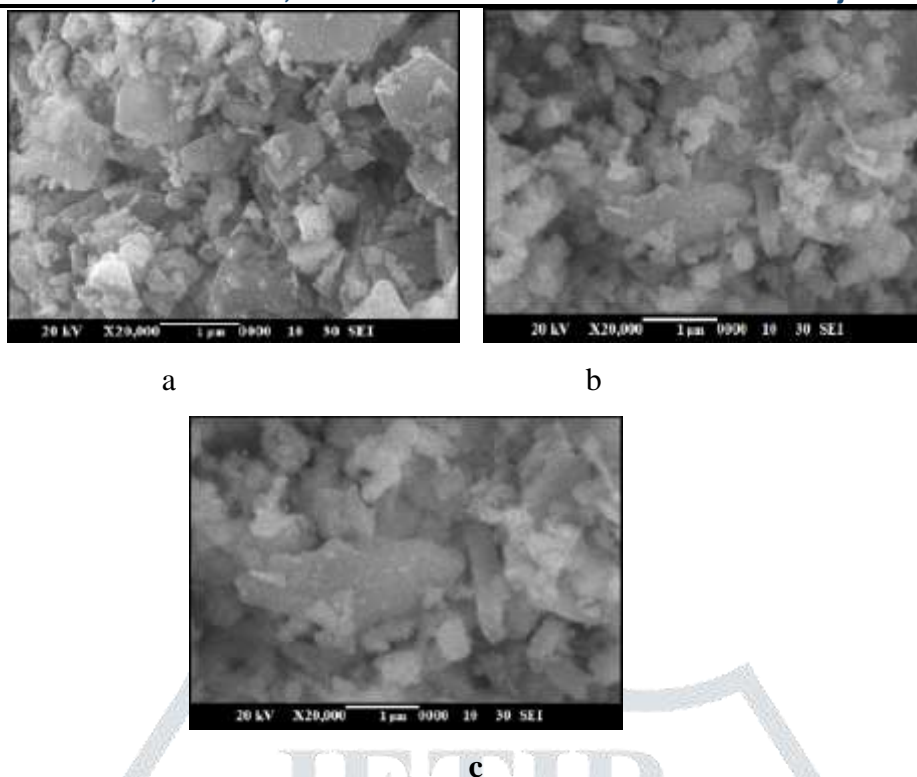


Figure.3(a-e) SEM of $Mg_{1-x}Mn_xFe_2O_4$ (where a, $x = 0.0$ b, $x = 0.5$ c, $x = 1.0$)

3.3 Fourier transforms infra-red study

The FTIR spectra of the $Mg_{1-x}Mn_xFe_2O_4$ were recorded in the range of 350–700 cm^{-1} are shown in **Figure 3**, which indicates presence of two fundamental absorption band groups. The band ν^1 corresponds to intrinsic stretching vibrations of the metal at the tetrahedral site, $M_{tetra} \leftrightarrow O$, where as ν^2 lowest band is assigned to octahedral-metal stretching, $M_{octa} \leftrightarrow O$ are shown in **Table 2**. It is known that the frequency is inversely proportional to the reduced mass. From **Table 2**, it is clear that the band ν^1 and ν^2 systematically decreases with increasing Mn^{2+} concentrations. The slight decrease of ν^1 and ν^2 with increase in Mn^{2+} may not only due to the difference in the ionic radius between Mn^{2+} and Mg^{2+} but also due to the difference of their masses in the A-site. The frequency ν^1 decreases with increases in manganese content indicating that Hook's law is obeyed.

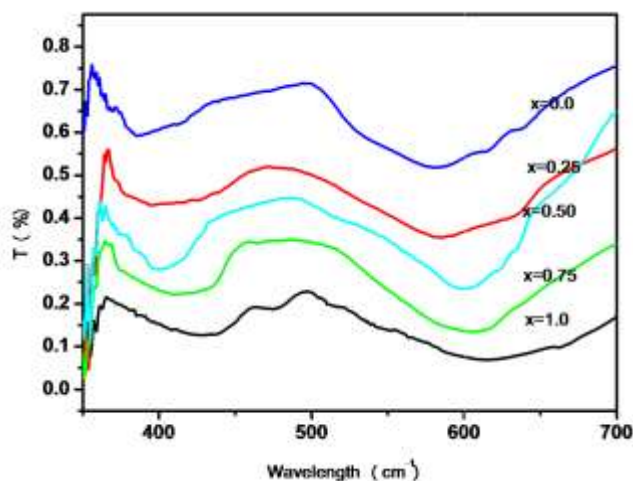


Figure.3. IR data for the system $Mg_{1-x}Mn_xFe_2O_4$

Table 2. Data of Positions of IR Absorption Bands in $Mg_{1-x}Mn_xFe_2O_4$ system.

Composition(x)	$\nu_1(\text{cm}^{-1})$	$\nu_2(\text{cm}^{-1})$
MgFe ₂ O ₄	584	383
Mg _{0.75} Mn _{0.25} Fe ₂ O ₄	586	388
Mg _{0.5} Mn _{0.5} Fe ₂ O ₄	591	396
Mg _{0.25} Mn _{0.75} Fe ₂ O ₄	604	405
MnFe ₂ O ₄	618	429

Conclusion

Nanocrystalline Mg_{1-x}Mn_xFe₂O₄ ($1.0 \geq x \geq 0$) was successfully synthesized by the sol-gel autocombustion route. The x-ray diffraction study reveals the formation of spinel phase. FTIR spectral studies indicated the two strong absorption bands, one around 600 cm⁻¹ (Tetrahedral) and the other weak around 500 cm⁻¹ (Octahedral). The content of the metals in the resulting spinel ferrites are close to the theoretical values as shown by EDAX measurements.

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