Influence of non-magnetic Zn-doping on the structural and the magnetic properties of magnesium ferrite

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Abstract. Spinel ferrites are the important class of soft magnetic material and are of interest to many researchers due to their excellent electrical and magnetic properties. Magnesium ferrite (MgFe₂O₄) is one such spinel ferrite with great potential technological applications. In the present study, the magnesium ferrite (Mg₀.₈Zn₀.₂Fe₂O₄) samples were prepared by well-known sol-gel auto-combustion method. The influence of Zn-doping on the structural and magnetic properties was investigated by X-ray diffraction and magnetization studies. The room temperature X-ray diffraction studies of the pure MgFe₂O₄ and Zn-doped Mg-Fe₂O₄ (Mg₀.₈Zn₀.₂Fe₂O₄) revealed the formation of single phase cubic spinel structure. The crystallite size obtained from Sherrer’s formula indicated that the Zn-doped and undoped shows nanocrystalline nature with crystallite size 22 nm and 24 nm respectively. The lattice constant (a) was found to be increased after Zn doping. Several other structural parameters are also increased after Zn doping. The magnetic properties were investigated by means of pulse field hysteresis loop technic. The M-H plot exhibits typical ferrimagnetic nature. The saturation magnetization increases after Zn doping. The observed magnetic behaviour of Mg₀.₈Zn₀.₂Fe₂O₄ nanocrystalline ferrite was on the basis of theoretical model.

1. Introduction

In the current decade, spinel ferrite nanoparticles have facilitated new advances in the field of nanoscience and nanotechnology [1]. These nanoparticles exhibits remarkable magnetic and electrical properties and are found to be useful in diverse potential application [2]. The nanoparticles of spinel ferrite have high surface to volume ratio [3], smaller size of the order of nanometre dimension [4], highly chemically stable [5], superparamagnetic [6] in nature and offers very good properties that can
be used in several applications. They can be prepared easily in nanosize form by several wet-chemical methods. These methods are simple, cost effective, required low temperature and produces homogeneous nanosize powder. The resultant yield is also much better than any other method. Many researchers have studied spinel ferrite for many applications. The excellent magnetic and electrical properties of spinel ferrite are sensitive to various factors such as synthesis method, synthesis parameters, synthesis conditions, nature and type of dopant [7]. All these factors are very much important and can be tuned according to the desired applications. The potential applications of these spinel ferrite nanoparticles are in electronic devices, magnetic resonance imaging (MRI) [8], magnetic recording media [9], drug delivery systems [10], ferrofluids [11], gas sensors [12], catalysis [13], antenna rods [14], storage devices, water purification [15] etc. In the family of spinel ferrite, magnesium ferrite [16] is a unique spinel ferrite which shows random spinel nature or partially inverse spinel structure. All such structural and physical properties of this Mg-ferrite depend on the preparation conditions and preparative parameters. Many researchers have investigated the electrical and magnetic properties of magnesium ferrite by doping various cations. Zinc is the non-magnetic in nature and may create interesting magnetic properties [17]. On doping of zinc in to magnesium at tetrahedral (A)-site, the magnetic properties were increased however there is a limit of zinc doping to enhance the magnetic properties. If the solubility limit of Zn doping is increased then the magnetic properties may be decreased. In view of the above facts, we focused the present investigation to the structural and magnetic properties of Mg-ferrite by doping of non-magnetic Zn ion (i.e. 20%). The results of X-ray diffraction and magnetic properties of MgFe$_2$O$_4$ and Mg$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ are discussed in the present paper.

2. Experimental

2.1 Raw Materials

Spinel structured Zn-doped magnesium ferrite (Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$) has been prepared by sol-gel auto-combustion method using citric acid as a fuel. AR grade magnesium nitrate (Mg(NO$_3$)$_2$), zinc nitrate (Zn(NO$_3$)$_2$), ferric nitrate (Fe(NO$_3$)$_3$·9H$_2$O) and citric acid (C$_6$H$_8$O$_7$) were used for the synthesis. Ammonia compound of nitrogen and hydrogen with the formula NH$_3$ was considered for maintaining pH of the solution of MgFe$_2$O$_4$ and Mg$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$.

2.2 Synthesis Method

Sol-gel auto-combustion method [19] was selected as the best for the present synthesis of nanocrystalline MgFe$_2$O$_4$ and Mg$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ ferrite. For the driving the sol-gel synthesis to the end reaction, metal nitrate to citric acid ratio was taken as 1:3. Initially, gradual form of (Mg(NO$_3$)$_2$) was added in deionized water to obtain clear solution of magnesium nitrate. Similarly, (Fe(NO$_3$)$_3$·9H$_2$O) and citric acid (C$_6$H$_8$O$_7$) were used for the synthesis. All the constituents of the gel form get burn to form a fluffy loose powder of Mg-Zn ferrite. This powder was grinded and annealed to form final product. Small pellets and powder form of Mg-Zn ferrite was used for characterization thereafter.

3. Characterization
3.1 X-Ray Diffraction

X-ray diffraction pattern of nanocrystalline MgFe$_2$O$_4$ and Mg$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ was taken by using Cu-κα radiation ($\lambda = 1.5405$ Å) on Philips PW-1730 X-ray diffractometer. The XRD parameters were characterized at room temperature. The entire X-ray diffraction pattern was recorded in 2θ range of 20° to 80° with a scanning rate of 0.02 deg/s and the major Bragg’s reflections of nanocrystalline Mg-ferrite were recorded for the analysis of structural parameters.

3.2 Magnetic property

The magnetic properties of the prepared MgFe$_2$O$_4$ and Mg$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ samples were measured using pulse field hysteresis loop technique at room temperature. From the M-H curve of MgFe$_2$O$_4$ and Mg$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$, the saturation magnetization ($M_s$), remanance magnetization ($M_r$) and coercive field ($H_c$) was to be found.

4. Results and discussion

4.1 Structural Properties

The prepared undoped MgFe$_2$O$_4$ and Zn-doped MgFe$_2$O$_4$ samples were studied for a structural characterization by X-ray diffractrometry. The phase purity, crystallite size (t) of the particles and lattice constant (a) etc. various structural parameters were calculated using XRD data on employing the related formulas. The following table 1 represents the Miller indices (hkl), (2θ), Sin θ, $sin\theta/\lambda$ interplannar spacing (d), and Intensity of various reflections of nanocrystalline Mg$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$.

| (hkl) | 2θ   | θ    | sinθ | $sin\theta/\lambda$ | d(Å) | I (a.u.) | I/I$_0$ |
|-------|------|------|------|----------------------|------|---------|--------|
| (220) | 30.252 | 15.13 | 0.261 | 0.1694 | 2.9519 | 3690.3 | 65.4   |
| (311) | 35.598 | 17.80 | 0.306 | 0.1984 | 2.5199 | 5645.3 | 100.0  |
| (222) | 37.86  | 18.93 | 0.324 | 0.2106 | 2.3744 | 3906   | 69.2   |
| (400) | 43.242 | 21.62 | 0.368 | 0.2392 | 2.0905 | 3865.5 | 68.5   |
| (422) | 53.634 | 26.82 | 0.451 | 0.2928 | 1.7074 | 3894   | 69.0   |
| (511) | 57.088 | 28.54 | 0.478 | 0.3102 | 1.6120 | 4528.4 | 80.2   |
| (440) | 62.638 | 31.32 | 0.520 | 0.3374 | 1.4819 | 5045.7 | 89.4   |
| (620) | 70.963 | 35.48 | 0.580 | 0.3768 | 1.3271 | 3964.1 | 70.2   |
| (533) | 74.18  | 37.09 | 0.603 | 0.3915 | 1.2773 | 4049.1 | 71.7   |

4.1.1 Lattice constant (a)

The lattice constant (a) of MgFe$_2$O$_4$ was calculated by the following relation in eq. [20];

$$a = d_{hkl}(h^2 + k^2 + l^2)^{\frac{1}{2}}$$

(1)
Where, \( a \) is the lattice constant, \( d \) is interplanar spacing and \( h, k, l \) are Miller indices. The lattice constant \( (a) \) of \( \text{MgFe}_2\text{O}_4 \) and \( \text{Zn} \)-doped \( \text{MgFe}_2\text{O}_4 \) samples (\( \text{Mg}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4 \)) was obtained to be 8.3413 Å, and 8.3552 Å which is in good agreement with the literature value.

### 4.1.2 Crystallite size (\( t \))

The crystallite size (\( t \)) of \( \text{Mg}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4 \) was calculated by using Debye-Scherrer method, which is mentioned by eq. \([21]\);

\[
t = \frac{K \lambda}{\beta \cos \theta} \tag{2}
\]

Where, \((t)\) is a crystallite size (nm), \( \lambda \) is a wavelength of X-ray (\( \lambda =1.5405 \) Å), \( \beta \) is broadening of peak at diffraction angle \( \theta \). \( \beta \) is measured using the equation \( \beta = (B^2 - b_0^2)^{1/2} \), where \( B \) is measured at full width at half maximum (FWHM) of the experimental profile and \( b_0 \) is an instrumental broadening. The crystallite size (\( t \)) of magnesium ferrite \( \text{MgFe}_2\text{O}_4 \) and \( \text{Mg}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4 \) samples was found to be 22 nm and 24 nm respectively, thus confirming the nanocrystalline nature.

### 4.1.3 X-ray density (\( d_\text{X} \))

The X-ray density (\( d_\text{X} \)) was calculated by the following relation \([22]\). The X-ray density for \( \text{MgFe}_2\text{O}_4 \) and \( \text{Zn} \)-doped \( \text{MgFe}_2\text{O}_4 \) was obtained as 4.577 (\( g/cm^3 \)) and 4.7461 (\( g/cm^3 \)). The values of crystallite size lattice constant (\( \alpha \)), unit cell volume (\( V \)) and X-ray density (\( d_\text{X} \)) are listed in table 2.

\[
d_\text{X} = \frac{8M}{N_A \alpha^3} \tag{3}
\]

Where, \( M \) is molecular weight and \( N_A \) is the Avogadro's number, \( \alpha \) is lattice constant.

| Composition ‘x’ | \( \alpha (\text{Å}) \) | \( d_\text{X} (g/cm^3) \) | \( V (\text{Å}^3) \) | Mol. Wt. \( g/m_\text{mol} \) | \( m/\text{mol} \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0.0             | 8.3413          | 4.5770          | 580.4           | 199.9590        |                 |
| 0.2             | 8.3552          | 4.7461          | 582.6           | 208.1600        |                 |

The values of tetrahedral site radius (\( r_A \)) and octahedral site radius (\( r_B \)) of the nanocrystalline \( \text{MgFe}_2\text{O}_4 \) and \( \text{Mg}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4 \) is reported in table 3.

| Composition ‘x’ | \( r_A (\text{Å}) \) | \( r_B (\text{Å}) \) |
|-----------------|-----------------|-----------------|
| 0.0             | 0.5726          | 0.7153          |
| 0.2             | 0.5751          | 0.7179          |

### 4.2 Magnetic Properties

Room temperature magnetic properties of nanocrystalline \( \text{MgFe}_2\text{O}_4 \) and \( \text{Mg}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4 \) were measured using pulse field hysteresis loop tracer technique applying magnetic field of 1000 Oe. The saturation magnetization (Ms), remanence magnetization (Mr) and coercivity (Hc) were determined.
as function of zinc concentration \( x \). For non-magnetic zinc doped Mg-ferrite, Néel's model of two sub-lattices does not hold good \[23\]. From the M-H curve, the saturation magnetization was reported as \( M_s = 28 - 44 \text{ emu/g} \), remanent magnetization (\( M_r = 10 - 14 \text{ emu/gm} \)) and coercive field (\( H_c = 250 - 210 \text{ Oe} \)). The behavior of coercivity in the \( \text{Mg}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4 \) spinel ferrite system can be explained on the basis of Brown's relation \[24\],

\[
H_c = \frac{2k_1}{\mu_0kM_S}
\]

(4)

Where, \( K_1 \) is anisotropy constant. Decrease in magneton number (\( n_B \)) (the saturation magnetization per formula unit in \( \mu_B \)) is associated with the decrease in A–B interaction and it is calculated using relation \[25\].

\[
n_B = \frac{(\text{mol. weight} \times M_S)}{5585}
\]

(5)

For \( \text{Mg}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4 \) samples, the increase in \( n_B \) \((1.0024 - 1.639 \mu_B)\) indicate the possibility of non-collinear spin structure in the system which can be explained on the basis of the three sub-lattice model suggested by Yafet Kittel \[26\].

Conclusions

We have successfully prepared nanocrystalline \( \text{Mg}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4 \) by using sol-gel auto-combustion method. The crystallite size (\( t \)) of the prepared \( \text{MgFe}_2\text{O}_4 \) and \( \text{Mg}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4 \) was recorded as 22 nm and 24 nm respectively. From the XRD data values it is cleared that; the prepared \( \text{MgFe}_2\text{O}_4 \) and \( \text{Mg}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4 \) belongs to the partially inverse; single phase; cubic spinel structure. Bragg’s angle (\( 2\theta \)) reflections are in very good agreement with the reported literature. X-ray density (\( d_X \)) was obtained as 4.577 (\( g/cm^3 \)) and 4.7461 (\( g/cm^3 \)). The lattice constant \( \alpha \) was reported as 8.3413-8.3552 (\( \text{Å} \)) for \( \text{MgFe}_2\text{O}_4 \) and \( \text{Mg}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4 \). The Room temperature magnetic parameters of nanocrystalline \( \text{MgFe}_2\text{O}_4 \) and \( \text{Mg}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4 \) such as saturation magnetization \( M_s = 28 - 44 \text{ emu/g} \), remanent magnetization (\( M_r = 10 - 14 \text{ emu/gm} \)) and coercive field (\( H_c = 250 - 210 \text{ Oe} \)) were recorded and found to be in good agreement.

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