Magnetic and structural studies of the Mn-doped Mg–Zn ferrite nanoparticles synthesized by the glycine nitrate process

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ABSTRACT

In this study, Nanocrystalline Mn–Mg–Zn ferrite with the chemical formula Mn_xMg_{0.5-x}Zn_{0.5}Fe_{2}O_4 (x=0, 0.1, 0.2, 0.3, 0.4, 0.5) was successfully synthesized by the glycine-nitrate auto-combustion process using glycine as a fuel and nitrates as oxidants. The as-synthesized powders were characterized by the X-ray diffraction analysis, field emission scanning electron microscopy, Fourier transform infrared spectroscopy (FTIR) and vibrating sample magnetometer. The X-ray diffraction data was used to determine the lattice constant, cation distribution and the oxygen position parameter. The results reveal that the nanocrystalline Mn–Mg–Zn ferrite has an average crystallite size of 35–67 nm and particle size of 40 nm. The lattice parameter increases linearly with an increase in the Mn content. The FTIR analysis confirms the intrinsic vibrational frequencies of the tetrahedral and octahedral of the spinel structure. The magnetic measurements indicate that the coercivity decreases, and the magnetization increases by increasing the Mn content.

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1. Introduction

Ferrites are the magnetic ceramics commonly used in the production of electronic components [1–4]. Among different types of ferrites, Mg–Zn ferrites represent an important class of soft-magnetic materials, which are widely used in computer memory and logic devices, cores of transformers, recording heads, antenna rods, loading coils and microwave devices, and so forth. As compared to other ferrites, they are preferable because of their high resistivity and low eddy current losses [5].

Recently, nanoparticle ferrites with a high surface to volume ratio have received much attention due to their useful, electrical and magnetic properties used in magnetic fluid, information storage and medical diagnostics [6,7]. These types of nanoparticles can be produced by different wet chemical methods, such as the co-precipitation [8], hydrothermal synthesis [9], micro-emulsion synthesis [7] and sol gel method [10]. In addition, various dry methods, including grinding [11], mechanical alloying [12] and thermal plasma methods [13] have been employed. Besides these methods, several attempts have been made using auto-ignited combustion reactions [14,15]. Among them, the glycine–nitrate process (GNP) is a simple, inexpensive and self-sustaining combustion synthesis technique, containing metal nitrates as oxidizers and glycine as fuel.

In this method, the aqueous solution begins boiling, afterward ignites, and an exothermal, self-sustaining and very rapid chemical reaction occurs [16]. The liberated heat can be utilized to provide the energy for phase transformation in synthesizing the desired products. In the combustion reaction the reaction temperature will not rise considerably. The reason can be attributed to the gas release and convection of heat loss. As a result, ultra-fine powders could be achieved to prevent both the over-growth of crystallites and the agglomeration of particles [16,17].

In addition, GNP has many other advantages, such as the fine particle size, high energy efficiency, fast heating rates, high compositional homogeneity, low-cost and fast method for preparing well-crystallized double oxides in about 30 min from preparing the precursor solution to obtain the final products [16,18]. The above-mentioned advantages enable GNP to be a promising candidate method for preparing nanostructure oxides [19]. In this area, several researches have investigated the magnetic properties of Ni_{0.5}Zn_{0.5}-ferrite by sol–gel and GNP methods. The results revealed that the saturation magnetizations for sol–gel and GNP methods are 14 and 22 emu/g, respectively [20,21]. The aim of this work is to study the structure and magnetic properties of Mg–Zn ferrite doped by Mn^{2+} ions. The replacement of nonmagnetic ion of Mg^{2+} by magnetic ion of Mn^{2+} (L=0, S=5/2, J=5/2) affects the magnetic properties. The angular momentum for Mn^{2+} is zero (L=0) which can reduce the magnetic coercivity. Mn^{2+} cation in spinel is at its high spin state (S=5/2). Its five d electron configurations are e^2t^2 and t^2g^2 at the tetrahedral and octahedral lattice site, respectively which can...
affect the saturation magnetization. It would be worth mentioning that as compared with the literature in this field [22–24], this paper has paid special attention to the synthesis of Mn–Mg–Zn ferrite by the GNP method.

2. Experimental method

Nanoparticles of $\text{Mn}_x\text{Mg}_{0.5-x}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (where $x=0, 0.1, 0.2, 0.3, 0.4, 0.5$ and named P1–P6, respectively) were synthesized by the auto-combustion synthesis method using glycine as a fuel and nitrates as oxidants. In an appropriate ratio, reagent grade $\text{Fe(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$, $\text{Zn(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}$, $\text{Mg(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$, $\text{Mn(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}$ and glycine ($\text{H}_2\text{NCH}_{2}\text{COOH}$) were used as starting materials. The metal nitrates dissolved in distilled water to obtain the precursor solution. A specified amount of glycine was then added into the nitrate solution at a molar ratio of 2:1 for fuel: oxidant (stoichiometric combustion). The mixed solution was put into a large beaker and heated on a hot plate to evaporate excess water until an auto-ignited and self-sustaining combustion occurred. The self-sustained combustion resulted in the fine Mn–Mg–Zn ferrite ash of brown in color.

X-ray diffraction (XRD) patterns of all samples were taken at room temperature by an X-ray diffractometer (Philips X’pert MPD), using a Co $\text{K}_\alpha$ radiation ($\lambda=1.789010\,\text{Å}$) at a voltage of 40 kV and a current of 30 mA. The XRD patterns of samples were recorded in the range $2\theta=10–90^\circ$ using a step size of 0.02$^\circ$ and a counting time of 2 s per step. The size and morphology of the particles were determined by field emission scanning electron microscope (FESEM, Hitachi, Japan S4160). The lattice parameters, the oxygen position and the cation distribution were determined by means of Rietveld refinement [25], using the reflex program [26]. For the calculation of the crystallite size, Scherrer’s method was applied [27]. Afterward the crystallite size was refined by Rietveld refinement. FTIR study was used to indicate the vibrational modes in the samples. The magnetic measurements of the prepared powder were determined at room temperature using the vibrating sample magnetometer (VSM) (Dexing, Model 250).

The Fourier Transform Infrared Spectroscopy (FTIR) spectrum was recorded as (KBr discs in the range 400–4000 cm$^{-1}$ using the (FTIR-Shimadzu-8000) spectrophotometer.

3. Results and discussion

3.1. FESEM

FESEM produces clearer, less electro-statically distorted images than conventional SEM. The shape, size and morphology of the samples were investigated by the field emission scanning electron microscope (FESEM) (Fig. 1). FESEM images reveal that the particles are approximately spherical in shape with the diameter between 35 and 45 nm and tend to agglomerate.

3.2. XRD analysis and cation distribution

The XRD patterns of the as-synthesized $\text{Mn}_x\text{Mg}_{0.5-x}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (where $x=0, 0.1, 0.2, 0.3, 0.4, 0.5$) shown in Fig. 2 confirm the formation of the single-phase spinel structure. To calculate the average crystallite size from the broadening of the XRD peaks of samples, the Rietveld refinement of the XRD pattern was applied. The goodness of fit was tested by means of values of $R_{wp}$, whose values were below 10%, indicating satisfactory fit [28], as shown in Fig. 3 for the P2 sample. Table 1 lists the refined crystallographic variables including crystallite size (D), chemical composition, lattice parameter (a), site occupancy, site coordination and oxygen positional parameter (3/8, 3/8, 3/8) ($u$).

![Fig. 1. FESEM micrograph of (a) p1 (b) p4 (c) p4 and (d) p6.](image-url)
cubic site symmetry m3m [29]. The refinement started with an ideal value of 0.25 for u. The shapes of the Bragg peaks were quantified by a pseudo-Voigt function. Each structure model was refined to convergence and the best result was selected on the basis of the various agreement factors of refinement. The distribution of the cations on two sub-lattices can be expressed as:

$$[\text{Mg}_{2}^{2+}\text{Mn}_{\beta}^{2+}\text{Zn}_{\gamma}^{2+}\text{Fe}_{1-\gamma}^{3+}]^{A}[\text{Mg}_{0.5-x-\beta}\text{Mn}_{\beta-x}\text{Zn}_{x}^{2+}\text{Fe}_{1+x-\beta}^{3+}]^{B}\text{O}_{4}$$

where the square practices contain the ions on the octahedral sites. In this formula, \(\alpha, \gamma, \gamma\) and \(\beta\) are constants refined by the Rietveld method and determine the cation distribution.

It is evident from Fig. 4 that with increasing substitution different cations have shown different nature of variation. The occupancy of Mn increases on both tetrahedral and octahedral sites with increasing its concentration. The population of other ions on the tetrahedral and octahedral sites shows different behaviour.

### 3.2.1. Particle size

The crystal growth in the solution depends on various parameters including extrinsic (molecular concentration of the material, pH and temperature) and intrinsic parameters (heat of formation, site preferences, electronic configuration). Both the above parameters can affect the growth process of the crystal. In this study the results show that with increasing the Mn content the particle size increase. This effect can be explained by the following points.

(i) Site preferences: It may happen that the grain growth is obstructed when the cationic preferences are not fully satisfied [30]. The dependence of the particle size on Mn concentration can also be related to the site preferences of Mn, Zn, Mg and Fe in ferrite structure. It is interesting to note that Zn\(^{2+}\) ions in the spinel structure have a very strong preference for tetrahedral sites, Mg\(^{2+}\) ions have a preference for octahedral site and Mn\(^{2+}\) ions have a preference for both octahedral and tetrahedral sites. Mn\(^{2+}\) is uniformly distributed amongst the different sites and therefore has a higher probability of being absorbed by a nucleus. Zn\(^{2+}\) forces Fe\(^{3+}\) to occupy octahedral site and it leads to the cationic preferences are not fully satisfied. Similarly, the restriction of Fe\(^{3+}\) to occupy only the octahedral sites as in the case of ZnFe\(_2\)O\(_4\) is no longer applied for MnFe\(_2\)O\(_4\) [30]. This accounts for higher particle sizes in Mn-doped ferrites, as compared to Zn-doped ferrites.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical composition</th>
<th>D (nm)</th>
<th>a (nm)</th>
<th>Site occupancy</th>
<th>Atomic coordinates (x-y-z)</th>
<th>Rwp (%)</th>
<th>Rp (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>Mg(<em>{0.5}) Zn(</em>{0.5}) Fe(_2) O(_4)</td>
<td>35.5</td>
<td>8.388</td>
<td>0.814 0.745 1.000</td>
<td>0.0000 0.6250 0.3832</td>
<td>8.60</td>
<td>5.91</td>
</tr>
<tr>
<td>P2</td>
<td>Mg(<em>{0.4}) Mn(</em>{0.1}) Zn(_{0.5}) Fe(_2) O(_4)</td>
<td>42.1</td>
<td>8.403</td>
<td>0.824 0.728 1.000</td>
<td>0.0000 0.6250 0.3833</td>
<td>8.14</td>
<td>5.80</td>
</tr>
<tr>
<td>P3</td>
<td>Mg(<em>{0.3}) Mn(</em>{0.2}) Zn(_{0.5}) Fe(_2) O(_4)</td>
<td>48.1</td>
<td>8.423</td>
<td>0.795 0.717 1.000</td>
<td>0.0000 0.6250 0.3795</td>
<td>7.05</td>
<td>5.22</td>
</tr>
<tr>
<td>P4</td>
<td>Mg(<em>{0.2}) Mn(</em>{0.3}) Zn(_{0.5}) Fe(_2) O(_4)</td>
<td>54.9</td>
<td>8.437</td>
<td>0.812 0.710 1.000</td>
<td>0.0000 0.6250 0.3812</td>
<td>7.09</td>
<td>5.10</td>
</tr>
<tr>
<td>P5</td>
<td>Mg(<em>{0.1}) Mn(</em>{0.4}) Zn(_{0.5}) Fe(_2) O(_4)</td>
<td>67.8</td>
<td>8.449</td>
<td>0.833 0.727 1.000</td>
<td>0.0000 0.6250 0.3818</td>
<td>6.53</td>
<td>4.82</td>
</tr>
<tr>
<td>P6</td>
<td>Mn(<em>{0.5}) Zn(</em>{0.5}) Fe(_2) O(_4)</td>
<td>65.1</td>
<td>8.465</td>
<td>0.822 0.723 1.000</td>
<td>0.0000 0.6250 0.3827</td>
<td>7.36</td>
<td>5.51</td>
</tr>
</tbody>
</table>
(ii) Enthalpy of formation: The presence of Mn promotes the crystal growth. The entropy of formation will reflect any configurational disorder present in the spinel, and at high temperature a considerable “entropy stabilization” may result from this disorder. The free energies of formation will be comparable to the enthalpy of formation for normal spinels and somewhat more negative for spinels with intermediate or inverse cation distributions [31]. The surface temperature affects the molecular concentration as an important factor in growing the tiny crystal at the surface of the crystal and hence the crystal growth. The formation of Mn-ferrite is more endothermic, as compared to the formation of other ferrites like Zn-ferrite. Thus, it is expected that should Mn be introduced in the system, less heat will be liberated, increasing the molecular concentration at the crystal surface and hence increasing the grain growth [31].

(iii) Electronic configuration and bonding energy: The increase in the particle size by the increase in Mn content may be explained by the electronic configuration of Mn$^{2+}$ (3d$^5$), and its more tendency to interact with ligands and oxygen anions, as compared to Mg$^{2+}$ 2S$^2$ 2P$^6$, which has a complete electronic configuration (noble gas). The lack of d electrons is important because there are very little covalent interaction and tendency toward extension between Mn$^{2+}$ and its ligand. Furthermore, it is reported by several researchers [32] that the smaller particle sizes of the samples doped with Zn ions are due to the lower bond energy of Zn$^{2+}$–O$^{2-}$ (159 kJ/mol) as compared with that of Co$^{2+}$–O$^{2-}$ (384 kJ/mol). In this line, the larger particle sizes of the samples doped with Mn ions are due to the higher bond energy of Mn$^{2+}$–O$^{2-}$ (946 kJ/mol) as compared with that of Zn$^{2+}$–O$^{2-}$ (159 kJ/mol) [33,34].

3.2.2. Lattice constant

As can be seen in Table 1 the lattice parameter increases from 8.388 to 8.465 nm with Mn$^{2+}$ concentration. The lattice constant was calculated using the relation $a = \sqrt{h^2 + k^2 + l^2}$ [35]. The "d" spacing values were calculated for the recorded peaks using Bragg's law, and the lattice constant (a) was calculated for the highest peak plane. From this table, it is clear that the experimental lattice constant and the crystallite size increase by increasing the Mn concentration. The Mn$^{2+}$ ion has a larger radius than most of the ions of the 3d$^5$ series, 0.080 nm instead of 0.064 nm (Mn$^{2+}$ = 0.080 nm, Mg$^{2+}$ = 0.072 nm, Zn$^{2+}$ = 0.074 nm, Fe$^{3+}$ = 0.064 nm in six-fold coordination). The noticeable increase in a up to $X_{Mn}$ = 0.3 relates to the higher tendency of Mn$^{2+}$ to go to the A site. To accommodate this larger cation, the lattice parameter is increased and hence some of the factors of the covalent bonding are reduced, thereby increasing the $N_{sp}$ coefficient (ferromagnetic double exchange).

3.3. FTIR analysis

Fig. 5 gives the IR absorption spectra of the investigated ferrite (x = 0–0.5). From this figure, it is found that the spectra consist of two significant absorption bands, first at about 600 cm$^{-1}$ and second at about 425 cm$^{-1}$. Absorption bands observed within this limit reveal the formation of the single phase spinel structure having two sub-lattices, tetrahedral (A) site and octahedral (B) site [36]. The absorption band, $v_1$, observed at about 600 cm$^{-1}$ is attributed to the tetrahedral site, whereas that of $v_2$ observed at about 425 cm$^{-1}$ is assigned to the octahedral group complexes. Furthermore, the FTIR spectra of the samples show bands at about 3415 and 1600 cm$^{-1}$, which are ascribed to the stretching modes and H–O–H bending vibration of the free or absorbed water. This suggests that hydroxyl groups are retained in the ferrites when they are prepared following the low temperature soft chemistry routes [37]. The bands at about 1384 and 570 cm$^{-1}$ are attributed to the stretching vibration of the anti-symmetric $\text{NO}_3^-$ and tetrahedral complexes of ferrite [38].

3.4. Magnetic properties

In spinel oxides, the magnetic moments are mainly from the parallel uncompensated electron spins of the individual ions. The magnetization curves of the Mn–Mg–Zn ferrite nano-particles measured at 27 °C are shown in Fig. 6. It is clear that the chemical composition can influence the magnetization curves as a result of a change in the particle size and distribution of cations. The nanoparticles provide excellent opportunities for the fundamental studies on the relationship between the magnetic behavior and the magnetic couplings at the atomic level.

Table 2 illustrates the dependence of the saturation magnetization on chemical composition. The $M_S$ value obtained for the samples varies between 48.59 and 65.25 emu/g at room temperature as the Mn content increases. This variation can be understood as follows.

(i) Size effect: As the Mn content increases the particle size and consequently the saturation magnetization increase. The existence of some degree of the spin canting (lack of full alignment of the spins in large applied fields) in the whole volume of the nanoparticles, the disordered surface/dead
layer and the spin-glass properties at the surface can explain the decrease of the saturation magnetization as the particle size decreases [39]. The dead magnetic layer originates from the demagnetization of the surface spin, causing the surface spins to be disordered or misaligned. This phenomenon weakens the total magnetization of the nanoparticles [39]. Basically, two mechanisms have been suggested to explain the origin of spin canting: one is the surface (or interface) effect, and the other is the finite-size effect. Variations in coordination numbers and distances of surface cations could result in a distribution of net exchange fields. Also, organic molecules bonded to the particles act as pinning centers for the spins at the surface.

(ii) Cation distribution: In the present work, by assuming 5 \( \mu_B \) for Fe(III) \((L=0, S=5/2, J=5/2)\), and 5 \( \mu_B \) for Mn(II) \( (L=0, S=5/2, J=5/2) \) [35], the net magnetic moment \((\mu/\text{molecule})=|M_A-M_B|\) is theoretically calculated, and the results are presented in Fig. 7. It is obvious that the magnetization of tetrahedral \((M_A)\) decreases; whereas the magnetization of octahedral \((M_B)\) and the net magnetization increase for the samples with higher Mn content. This can be attributed to the higher concentration difference of magnetic ions \((\text{Fe}^{3+} \text{ and Mn}^{3+})\) in octahedral and tetrahedral sites by assuming the collinear ferrimagnetic spin structure. Consequently, the Fe–Fe and Mn–Mn interactions are increased due to an increase in the concentration of Fe and Mn ions on the B-sites.

It appears that the substitution of magnetic Mn has strengthened the ferrimagnetic interactions in the system causing an increase of magnetic order with increasing its concentration \((x)\). Since, because the occupancy of magnetic Mn increases with \(x\) on both tetrahedral and octahedral sites, the net magnetization increases relatively significantly. The synthesis method can affect strongly the particle size and cation distribution. These parameters change the magnetic properties like saturation magnetization and coercivity. For this reason, it is clear that, a magnetic powder obtained by GNP method may be have different magnetic properties as compared with other methods [20,21].
The magnetic coercivity of the particles depends significantly on their magneto-crystalline anisotropy, micro-strain, inter-particle interaction, temperature, size and shape [40]. Mg$^{2+}$ ($2S^2 2P^6$) and Mn$^{2+}$ ($3d^5$) do not have contribution in angular momentum (l=0), magneto-crystalline anisotropy and/or lattice-spin coupling. For this reason, the reduction in magnetic coercivity from 67.7 to 52.4 Oe Table 2 can be contributed only to the increase in the particle size ($H_{c} \propto D^{-1}$) and/or the decrease in the saturation magnetization ($H_{c} \propto M_{s}$) [40].

### 4. Conclusions

In this paper, Mn–Mg–Zn ferrite powders were synthesized by the glycine-nitrate process. The data obtained from XRD, FESEM, FTIR and VSM revealed that:

1. The nanocrystalline Mn–Mg–Zn ferrite shows the absorption bands near 600 and 400 cm$^{-1}$, respectively. The high frequency band around 600 cm$^{-1}$ is attributed to the tetrahedral complexes and the band near 400 cm$^{-1}$ corresponds to the octahedral complexes.
2. To calculate the average crystallite size from the broadening of the XRD peaks of samples and other micro-structural properties, the Rietveld refinement of XRD pattern was applied.
3. As the Mn content increases, the lattice parameter due to its high ionic radius and incomplete-symmetry electronic configuration.
4. As the Mn content increases, the crystallite size increases as a result of site preferences, enthalpy formation, electronic configuration and bond energy.
5. Cation site preferences have also caused a large variation in the magnetic ion concentration over the two sublattices giving rise to significant change in the strength of sublattice magnetic moments.
6. The saturation magnetization increases due to an increase in the particle size and an increase in the difference in the saturation magnetization of two sub-lattices.
7. As the Mn content increases, the magnetic coercivity decreases as a result of an increase in the saturation magnetization and the particle size. Furthermore, Mg$^{2+}$ ($2S^2 2P^6$) and Mn$^{2+}$ ($3d^5$) do not have contribution in angular momentum and magneto-crystalline anisotropy.

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_s$(emu/g) $\pm$ 0.01</th>
<th>$H_c$(Oe) $\pm$ 0.01</th>
<th>$M_r$(emu/g) $\pm$ 0.01</th>
<th>$H_{max}$(kOe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>48.59</td>
<td>67.71</td>
<td>7.46</td>
<td>13.6</td>
</tr>
<tr>
<td>P2</td>
<td>53.98</td>
<td>64.89</td>
<td>7.9</td>
<td>13.5</td>
</tr>
<tr>
<td>P3</td>
<td>55.14</td>
<td>63.47</td>
<td>8.08</td>
<td>13.9</td>
</tr>
<tr>
<td>P4</td>
<td>58.27</td>
<td>60.13</td>
<td>8.45</td>
<td>13.7</td>
</tr>
<tr>
<td>P5</td>
<td>59.74</td>
<td>57.35</td>
<td>8.5</td>
<td>13.7</td>
</tr>
<tr>
<td>P6</td>
<td>65.25</td>
<td>52.39</td>
<td>8.86</td>
<td>13.6</td>
</tr>
</tbody>
</table>

Fig. 6. M–H curves of powders.

Fig. 7. Variation of the sublattice and net magnetic moments at room temperature with Mn concentration.
Acknowledgements

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