Effect of Ni Substitution on Structural and Magnetic Properties of Mn-Zn Ferrite Nanoparticles

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Abstract

The nickel substituted Mn-Zn spinel ferrite system has been prepared by sol-gel method. The XRD patterns confirm the synthesis of single phase ferrite nanoparticles for all the samples. The lattice parameter and the distance between magnetic ions for each A-site and B-site were found to decrease with increasing nickel content. The crystallite size of the samples was determined from XRD and found in the range of 29-37nm. The B-H loop parameters, g-value, linewidth ΔHv, resonance field have been investigated at room temperature. It has also been observed that saturation magnetization increases up to x=0.1 and then decreases. The EPR study reveals the super paramagnetic nature of the materials.

Introduction

The nanoparticles with unique magnetic properties and their pledging technological applications have attracted considerable attention in the recent years [1]. Soft ferromagnetic oxides are of great importance as high-frequency magnetic materials. The general formula for these compounds is MFe$_2$O$_4$, where M is a divalent metal ion such as Fe$^{2+}$,Ni$^{2+}$,Mg$^{2+}$,Mn$^{2+}$,Zn$^{2+}$,Cu$^{2+}$ etc. or a mixture of these ions [2]. Through the choice of various divalent cations in the ferrites, the magnetic properties can be tuned and customized according to technological applications [3].

Mn-Zn ferrite nanoparticles have a wide range of magnetic applications such as recording heads, transformer cores, and noise filters etc. because of their superior magnetic properties such as high saturation magnetization and high initial permeability [4, 5]. Mn-Zn ferrites are usually limited to frequencies <500 kHz due to their relatively low resistivities (0.02-20 Ωm) [6], and in consequence, these ferrite nanoparticles are not suitable for magnetic applications at higher frequencies due to high eddy current losses. Ni-Zn ferrite nanoparticles have many attractive properties and a wide range of technological applications such as low and high-frequency transformer cores, antenna rods and microwave devices due to their low eddy currents and dielectric losses, inferior magnetic properties at higher frequencies limit their use [7]. Through the suitable combination of Mn-Zn and Ni-Zn ferrite nanoparticles, a material can be achieved with not only high resistivity but also appreciative magnetic properties. This is suitable for magnetic applications at higher frequencies with minimum power losses due to eddy currents [5, 8].

Experimental

Materials & Methods

Nanoparticles of Mn$_{0.5}$Ni$_x$Zn$_{0.5}$Fe$_2$O$_4$ (x=0.0, 0.1, 0.2, 0.3) have been prepared by a sol-gel method using analytical grade metal chlorides as starting materials. In this process, for sample x=0, 1.7158 g of manganese chloride, 1.4447 g of nickel chloride, 2.1442 g of zinc chloride, and 2.3557 g of iron chloride were dissolved in 100 ml of distilled water to get a clear solution. The mixtured was adjusted between 6 and 7. During heating, ethylene glycol has been also added in the mixture for homogeneity. During evaporation, the solution becomes viscous and finally formed a very viscous brown gel. The gel was then dried in an oven at 250°C for 12 hours, and then it is crushed into fine powder form. The as-prepared powder then annealed at 800°C for 2 hours and sintered at
1000°C for half an hour. The obtained materials were characterized by X-ray diffraction (XRD) using Bruker Diffractometer with Cu Ka radiation source at room temperature and collected the data for every 0.017° in the angle range 2θ=90° of 2θ. The magnetization measurements were done at room temperature up to a maximum field of 2 Tesla, using Vibrational Sample Magnetometer (VSM), Electron Spin Resonance (ESR) spectra were taken by using an X-band Varian’s E-112 ESR spectrometer. SEM images were recorded by using Hitachi E-1010 type Scanning Electron Microscope.

**Results and Discussion**

**XR D and SEM Study**

The XRD patterns of the samples are shown in Fig. 1, which confirmed the formation of cubic spinel structure and showing that all the samples are formed in pure phase, as indexed by using JCPDS. The diffraction peaks consist of (220), (311), (222), (400), (422), (511), (440), (531) and (622) planes as shown in Fig. 1. The broad XRD peaks are an indication of reduced particle size of the as-prepared material. In addition to the ferrite peaks, impurities peaks corresponding to α-Fe2O3 have been observed in the XRD patterns of the samples. Probably at increased annealing temperature Fe gets converted into its oxide and the extra peaks are due to the formation of α-Fe2O3 [14]. The morphology of powder shown in Fig. 2 is porous and agglomerated. This morphology is like that reported by Gholam Reza Mershakari et al. [28]. The fluffy nature and voids in the sol-gel prepared powder are due to large amount of gases evolved during the reaction.

The average crystallite size \( D \) has been calculated by using Scherrer formula [15].

\[
D = \frac{k \lambda}{\beta \cos \theta}
\]

(1)

Where \( k \) is constant, related to the crystallite shape, normally taken as 0.9 [16], \( \lambda \) is the wavelength of X-ray, \( \beta \) is the full width at half maximum (FWHM) of XRD peak and \( \theta \) is the Bragg angle for the actual peak. The lattice parameter \( a \) has been calculated by using the relation [17].

\[
a = d_{002} \sqrt{h^2 + k^2 + l^2}
\]

(2)

Where \( d_{002} \) is the interplanar separation and \( h,k,l \) are Miller indices of the plane.

The XRD density \( (\rho) \) has been calculated according to the relation [18]

\[
\rho = \frac{M}{Na^3}
\]

(3)

Where ‘N’ is the Avogadro’s number, ‘M’ is the molecular weight of the sample and ‘\( a \)’ is the lattice constant.

The crystallite size has been calculated from the XRD line width of the (311) peak using equation (1). The values of structural parameters are listed in Table 1.

<table>
<thead>
<tr>
<th>Ni Content</th>
<th>Observed Crystallite size (nm)</th>
<th>Rep.</th>
<th>Lattice Parameter(Å)</th>
<th>Crystallite Density(g/cc)</th>
<th>La (Å)</th>
<th>Lb (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0.0</td>
<td>34.58</td>
<td>14</td>
<td>8.425</td>
<td>8.401</td>
<td>5.258</td>
<td>5.336</td>
</tr>
<tr>
<td>x=0.1</td>
<td>31.94</td>
<td>13.5</td>
<td>8.414</td>
<td>8.390</td>
<td>5.285</td>
<td>5.272</td>
</tr>
<tr>
<td>x=0.2</td>
<td>29.25</td>
<td>14</td>
<td>8.355</td>
<td>8.374</td>
<td>5.487</td>
<td>5.311</td>
</tr>
<tr>
<td>x=0.3</td>
<td>36.48</td>
<td>15.2</td>
<td>8.337</td>
<td>8.368</td>
<td>5.545</td>
<td>5.150</td>
</tr>
</tbody>
</table>

For the unsubstituted sample, 80% of manganese ions occupy the tetrahedral (A-site) position, while the remaining, 20% occupy the octahedral (B-site) position. Zinc and nickel ions prefer to occupy the tetrahedral (A-site) and octahedral (B-site) respectively, while iron ions occupy both tetrahedral (A-site) and octahedral (B-site), it prefers the octahedral (B-site) [19]. It has been observed that both crystallite size and lattice parameter decrease as an increase in nickel ion substitution. This can be explained on the basis of the relative ionic radius. The ionic radius (0.82Å) of Mn2+ ions is larger than the ionic radius (0.69Å) of theNi2+ ion. Due to the replacement of smaller Ni2+ ions for larger Mn2+ ions in the lattice, the unit cell contracts preserving the cubic symmetry. Though the crystallite size of the sample is found to be minimum with nickel substitution x=0.2. For substitution x=0.3, a significant fraction of Mn2+ and Zn2+ occupies the B-sites and forces Fe3+ to the A-sites against their chemical preferences. The ionic radius (0.69Å) of Ni2+ ions is larger than the ionic radius (0.64Å) of Fe3+ ions. Due to the replacement of Ni2+ ions for Fe3+ ions in the sample, the unit cell expands while preserving the cubic symmetry and hence crystallite size increases.

The crystallite sizes and lattice parameters are decreased with increasing Ni substitution, as shown in Fig. 3 and 4. The values of lattice parameters have been observed in the range 8.414 Å to 8.373 Å, are in good agreement with those of C. Venkataraju et al. [20], S. G. Dahotre et al.[21]. The XRD density increases with increase in Ni content and
decrease in Mn content. This increase in XRD density (ρn) is a direct effect of the lattice parameter. The effect of the Mn²⁺ concentrations on the microstructure of ferrites has been reported by M. F. Yan and D. Johnson [22].

A Globus et al. [23] reported that distance between magnetic ions (jump length ‘L’) of the electrons affects the fundamental properties in ferrites. The distance between magnetic ions (jump length ‘L’) for each tetrahedral (A-site) and octahedral (B-site) i.e. ‘L-A’ and ‘L-B’ respectively has been calculated from the following relations [24].

\[ L_A = \frac{\sqrt{3}}{4} a \]  
\[ L_B = \frac{\sqrt{2}}{4} a \]

Where, ‘a’ is the lattice parameter.

Both the jump length ‘L-A’ and ‘L-B’ are directly proportional to the lattice parameter ‘a’. Hence, it has been observed that both ‘L-A’ and ‘L-B’ were found to be decreased with increase in nickel substitution (x) as shown in Table 1.

### Magnetic Studies

Magnetizations of the as-prepared samples have been measured using a VSM at room temperature. The hysteresis curves of Mn₂₋ₓNiₓZn₀.₅Fe₂O₄ (x=0.0, 0.1, 0.2, 0.3) ferrite nanoparticles are shown in Fig. 5 and magnetic parameters are presented in Table 2. It has been observed that all the samples exhibited narrow hysteresis loops, with a behavior characteristic of soft magnetic materials [25].

The magnetic moment per formula unit (nB) in Bohr magneton (µB) was calculated by using the following equation [26].

\[ n_B = \frac{M_{sat} \times M_1}{5585} \]

Where \( M_{sat} \) is the molecular weight of the sample and \( M_1 \) is the saturation magnetization in the electromagnetic unit.

It has been observed that the magnetization of all the samples increases with increasing applied magnetic field that attains saturation magnetization up to the field 6000 Gauss. Similar observations at room temperature, magnetizations have been reported by C. Venkataramu et al. [20] and K. Jalal et al. [27]. It has been also observed that as the Ni ion concentration increases, nickel goes to B-site and transfer Fe³⁺ ions from B-site to the A-site [28]. Thus increase in the magnetization of the A-sublattice is expected. The increasing iron content at A-site results in the A-B interaction gradually increases, as experienced by the B-site iron ions and this reduces the canting of spins of B-site iron ions. Therefore the magnetization of the A-sublattice increases. At the same time, decreased iron contents at B-site reduce the magnetization of the B-sublattice. The net magnetic moment (M) is the sum of the magnetization of A and B-sublattices, i.e. \( M = M_A - M_B \). Hence the net magnetization decreases. The initial increase in magnetization has been observed, which is due to dominant effects of spin canting over the combined effects of increase and decrease of iron ions at A and B sites respectively [29]. However for composition x=0, i.e. for higher Mn²⁺ ion concentrations, more Fe³⁺ ions being at B-site, the increased B-B interaction decreases the magnetization of the B-site. D.R.Mane et al [30] reported magnetic properties to alter significantly due to the formation of FeO₃ as a result of zinc loss. The variation of magnetization with Ni content is shown in Fig. 6.
The Stoner-Wohlfarth model which explained Coercivity value as:

\[ H_c = \frac{2K}{\mu_0 M_s} \]  

(7)

Where K is the anisotropy constant, \( \mu_0 \) is the universal constant of permeability at free space and \( M_s \) is the saturation magnetization. According to this model, Coercivity is inversely proportional to the saturation magnetization [31]. The variation of coercivity with Ni content is shown in Fig. 7. For all the substitutions, the Ni\(^{2+}\) ions system may be deliberated as hidden. This may interpret the almost linear dependence of K on Ni\(^{2+}\) ion concentration. It has been observed that the anisotropy constant \( (K) \) increases with increase in Ni\(^{2+}\) ion concentration. The anisotropy constant of ferrites is interpreted by the one-ion model. It is also known that the anisotropy field in ferrite nanoparticles results from the presence of Fe\(^{2+}\) ions [32]. It is generally recognized that in ferrites, electron exchange between Fe\(^{2+}\) and Fe\(^{3+}\) ions on B-sites is due to dominant conduction mechanism [33]. Apparently, with an increase in Ni substitution, Fe\(^{2+}\) ion concentration increases as a result anisotropy constant \( (K) \) increases. The variation of anisotropy constant \( (K) \) with Ni content is shown in Fig. 8.

EPR Study

The EPR spectra of as-prepared samples have been recorded by scanning the magnetic induction at 9.1 GHz and microwave frequency at room temperature. EPR spectroscopy technique is used to investigate the various magnetic parameters such as resonance linewidth \((\Delta H_{pp})\), Resonance field \((B)\) and Lande's splitting factor \((g)\)-value of \(\text{Mn}_{0.5}\text{Ni}_{x}\text{Zn}_{0.5}\text{Fe}_{2}\text{O}_4\) ferrite nanoparticles and the values are listed in Table 3. All the spectra have been analyzed by using Lorentzian distribution function.

<table>
<thead>
<tr>
<th>Ni Content ((x))</th>
<th>Linewidth ((\Delta H_{pp})) Gauss</th>
<th>Resonance Field ((B)) Gauss</th>
<th>(g)-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>627</td>
<td>3140</td>
<td>3341</td>
</tr>
<tr>
<td>0.1</td>
<td>485</td>
<td>3210</td>
<td>3345</td>
</tr>
<tr>
<td>0.2</td>
<td>464</td>
<td>3225</td>
<td>3346</td>
</tr>
<tr>
<td>0.3</td>
<td>548</td>
<td>3155</td>
<td>3280</td>
</tr>
</tbody>
</table>

The \(g\)-value is a function of the molecular motion, the symmetry of the ions and the paramagnetic properties, which is also a constant of proportionality between the field and frequency. The \(g\)-value is calculated by the relation [36].

\[ g = \frac{h \nu}{\beta H} \]  

(8)

Where, \( h \) is Planck’s constant, \( \nu \) is the microwave frequency, \( \beta \) is Bohr magneton and \( H \) is the magnetic field at the resonance.

The EPR is important for investigating the magnetic properties of ferrites. The linewidth of EPR signal for any ferrite material generally originated from two sources: (i) magnetic dipole-dipole interactions among particles and (ii) Interparticde superexchange interactions between magnetic ions through oxygen ions. Superexchange interaction becomes stronger when the distance between metallic and oxygen ions are smaller and the angle between these two bonds is nearer to 180\(^\circ\). Linewidth may get broadened or narrowed depending upon the interaction inside the material. The large linewidth and \(g\)-value rise due to leading dipole-dipole interactions while the small linewidth and \(g\)-value rise due to leading superexchange interactions [37].

The increase in nickel content affects the increase in motion of electrons, which consequence in stronger superexchange interaction amidst cations and oxygen ions which reduces linewidth and \(g\)-value [38]. For the substitution \(x=0.3\), the broad linewidth and the reduced resonance field estimates can be assigned to surface spin disrupt probably due to anti ferromagnetic interactions among the adjoin spins in the magnetic grains [39].

It has been observed that the resonance field \((B)\) increases with Ni content up to substitution \(x=0.2\) and then decreases. The variation of the resonance field \((B)\) with Ni content is shown in Fig. 9. It is also observed that both the linewidth \((\Delta H_{pp})\) and \(g\)-value decrease with increasing Ni substitution up to \(x=0.2\) and then increase. The variations of the linewidth \((\Delta H_{pp})\) and \(g\)-value with Ni content are shown in Fig. 10 & 11, respectively.
The smaller values of linewidth and g-value in the present work may be due to dominant super exchange interactions between cations and oxygen ions. C. Venkataraju et al. [40] have observed the peak-to-peak linewidth of the EPR spectra of Mn_{0.75}Ni_{0.25}Fe_{2}O_{4} (x=0, 0.1, 0.2, 0.3) in the range of 537-346 Gauss. It has been observed that the increased peak-to-peak linewidth of the EPR spectra of the samples in the range of 627-464 Gauss is due to the appearance of α-Fe_{2}O_{3} [41].

Conclusions
We have investigated structural and magnetic properties of sol-gel prepared Mn_{1-x}Ni_{x}Zn_{0.5}Fe_{2}O_{4} (x=0.0, 0.1, 0.2, 0.3) ferrite nanoparticles. The X-ray diffraction pattern confirms the single-phase ferrite nanoparticles for all the samples. Both crystallite size and lattice parameter have been observed to decrease with increase in nickel substitution. The saturation magnetization is maximum of the sample for x=0.1 and then decreases with the increase of nickel substitution. The linewidth and g-value decreases with increase in nickel content up to x=0.2 and then increases. This may be due to increase in superexchange interactions among cations and oxygen ions and this can be interpreted by spin-spin and spin-lattice relaxation models. SEM images indicate the morphology of the powders is agglomerated and porous.

Acknowledgements
The Author would like to thank Dr. S. G. Dahotre and, Dr. U. L. Shinde for the co-operation in preparing the samples and IIT Bombay for characterization of the samples.

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