A study on structural and magnetic properties of Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ (0 $\leq x \leq 0.6$) ferrite nanoparticles

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A series of nickel doped zinc ferrite Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ (0 $\leq x \leq 0.6$) nanoparticles were prepared using sol-gel method. The influence of Ni$^{2+}$ ions substitution on the structural and magnetic properties of ZnFe$_2$O$_4$ spinel ferrites were subsequently studied. The XRD patterns of as synthesized samples confirm the single crystalline phase formation without any trace of impurity. The lattice parameter decreases linearly from 8.368 Å to 8.264 Å, whereas crystallite size increases with the increase in Ni$^{2+}$ ion concentration. HRTEM images also confirm the nano size particle formation. From the HRTEM images this has been observed that the particle size lies in the range 15-45 nm. The saturation magnetization increases from 26.70 emu/gm for $x = 0.0$ to 45.85 emu/gm for $x = 0.4$ with the increase in nickel content. The increase in saturation magnetisation is also supported by spin concentration values as calculated from EPR study.

Keywords: Zinc ferrite, sol-gel, saturation magnetization and spin concentration.

INTRODUCTION

The magnetic nanoparticles have remarkable increasing interest in the recent decades both in technical and academic fields because of their special properties as compared with bulk materials. The nanomaterials exhibit unusual properties like superparamagnetism, spin canting and surface anisotropy due to which they have potential application in high density magnetic storage, electronic and microwave devices, transformer cores, telecommunication equipments, ferrofluids, magnetically guided drug delivery and gas sensors [1-7]. Ferrites are ceramic ferromagnetic materials with general chemical formula MeFe$_2$O$_4$, where Me represents metallic cations like Fe, Mg, Mn, Ni, Co, Zn, Cu or a mixture of these. These nanoparticles crystallize into the spinel structure in which the sites occupied by the cations are of two types, tetrahedral and octahedral sites. Nickel and Zinc are known to have strong preference for the tetrahedral and octahedral sites, respectively, making nickel ferrite a model inverse spinel ferrite and zinc ferrite a model normal ferrite. However, the composite Ni–Zn ferrites are known to exist as mixed spinel structure. The compositional variation in these ferrites results in the redistribution of metal ions over the tetrahedral and octahedral sites which can modify the properties of ferrites. The physical properties of these ferrite nanoparticles can be also tailored by changing the parameters such as composition or by the synthesis method. There are various methods for the synthesis of ferrite nanoparticles which includes sol-gel, oxidation, hydrothermal, ball milling and chemical co-precipitation method [8-12]. Out of these methods, sol-gel method is best method for the preparation of the nanoparticles because it maintains the stoichiometry of the starting components and prevents the presence of contamination and other impurities. In view of above, present study focuses on the doping effect of Ni$^{2+}$ ions on the structural, morphological and magnetic properties of ZnFe$_2$O$_4$ ferrites nanoparticles.

EXPERIMENTAL

Nanocrystalline Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ ($x = 0.0$, 0.2, 0.4 and 0.6) ferrite nanoparticles have been synthesized by sol-gel method. In this method, stoichiometric ratios of Ni(NO$_3$)$_2$·6H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O were dissolved in minimum amount of ethylene glycol at room temperature and the sol was heated at 80 °C with constant stirring to form a wet gel. The gel was then dried overnight at 100 °C to form Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ ferrite powder. The powder was further ground for about an hour and was used for further characterizations. For structural investigations as prepared samples were characterized by X-ray diffractometer (XRD) and high resolution transmission electron microscopy (HRTEM). XRD measurements were carried out using Rigaku make powder X-ray diffractometer with Cu K$_\alpha$ radiation (λ = 1.54 Å) in the 20 range from 20° to 70° with a step size of 0.02°/s. The morphology and shape of synthesized nanoparticles were studied with the help of high resolution transmission electron microscope (HRTEM) (model TECNAI F-30). The magnetization measurements on these samples were carried out by search coil method. Further, Varian E Line...
Century X-band EPR spectrometer (Model-E-112) was used for EPR measurements. The measurements were done at 9.36 GHz with modulation frequency 100 kHz at room temperature.

RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction pattern of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6$) samples. The XRD patterns were analyzed by comparing it with standard JCDPS card. The $d$ values and intensities of observed diffraction peaks matches well with JCPDS card no. 52-0278 of the nickel zinc ferrite having Fd-3m space group. X-ray diffraction pattern shows broad peaks indicates the ultra fine nature of the particles and lower crystallinity. The XRD pattern shows that peaks shifts towards higher angle side with increase in Ni$^{2+}$ ion concentration. The lattice parameter of as-prepared sample, according to the cubic crystal structure was calculated from the main peak of spinel structure (311) using equation:

$$a = d\sqrt{h^2 + k^2 + l^2}$$  \(1\)

where “$d$” is the interplanar distance, “$h, k$ and $l$” are the miller indices and “$a$” is the lattice parameter [13]. It is observed that lattice parameter decreases from 8.368 Å to 8.264 Å with nickel ion concentration which may be attributed to the smaller ionic radii of Ni$^{2+}$ ions (0.78 Å) as compared to Zn$^{2+}$ (0.82 Å) cations [14,15]. The induced strain in the crystallites has been calculated. It is found that strain is maximum in the zinc rich sample and decreases as nickel ion concentration increases. The values of the strain are listed in Table 1.

The average crystallite size ($D$) was calculated from the full width at half maximum (FWHM) of (311) peak by using Scherrer’s equation [16]

$$D = \frac{k\lambda}{\beta \cos \theta}$$  \(2\)

Where $k = 0.89$, $\lambda$ is the wavelength of CuK$\alpha$ (1.54 Å), $\beta$ is the peak FWHM measured in radians and $\theta$ is the angle of Bragg diffraction. All the structural parameters calculated from the diffraction pattern are listed in Table 1. The variation of crystallite size and lattice parameter with nickel ion concentration is shown in Fig. 2. The crystallite size is found to increase with the increase in Ni content. The X-ray density $d_x$ is calculated using the relation [17, 18]

$$d_x = \frac{8M}{Na^3}$$  \(3\)

where $M$, $N$ and ‘$a$’ are the molecular weight, Avogadro’s number and lattice parameter respectively and tabulated in Table 1. X-ray density increases linearly with the increase in nickel ions concentration since nickel ions (0.78 Å) have smaller ionic radii than zinc ions (0.82 Å).

HRTEM provides further insight into the morphologies and structural details of these samples. Fig. 3 shows the HRTEM images of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ samples ($x = 0.2$, $0.6$) samples. The observed size of ferrite nanoparticles by HRTEM micrograph exhibit the similar trend with the size calculated by Debye-Scherer formula. The HRTEM images show the almost all the particles are spherical in shape and particles size increases lies in the range 15-45 nm. The slight agglomeration of the nanoparticles has been observed from the HRTEM micrographs which may be due to the Vander Waals forces and magnetic interaction between these magnetic nanoparticles [19].

The Magnetic characterization of the samples was performed by search coil method at room temperature. Fig. 4 displays the magnetization curves for various compositions of nickel substituted...
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It is observed from the magnetization curve that the substitution of Ni$^{2+}$ ions in the host lattice has increased the domain magnetization of the samples. The increase of saturation magnetization with nickel content can be due to many factors like cation distribution, the existence of surface spin or the formation of spin glass structure etc. The increase in saturation magnetization value with nickel ion concentration is due to the larger magnetic moment of nickel ion as compared to zinc ions [20, 21]. Variation of saturation magnetization ($M_s$) depends on the distribution of cations on tetrahedral and octahedral sites in spinel lattice. The cation distribution of Ni–Zn ferrites is given by [22] $[\text{Zn}^{2+}]_{1-x} \text{Fe}^{3+}_x [\text{Ni}^{2+}]_x [\text{Fe}^{3+}]_y [\text{Fe}^{3+}]_z$. It shows that all the Zn ions occupy tetrahedral (A) sites, Ni ions occupy octahedral (B) sites and Fe$^{3+}$ ions are distributed between tetrahedral and octahedral sites. The smaller value of saturation magnetization for samples with less nickel content may be due to lattice defects, weaker magnetic superexchange interactions between Tetrahedral (T-sites) and Octahedral (O-sites) and random orientation of spin on the surface of the nanoparticles [23]. The ferromagnetic nature of these samples is also confirmed from the magnetization curve. The saturation magnetization increases from 26.70 emu/gm ($x = 0$) to a value of 45.85 emu/gm ($x = 0.4$).

EPR spectroscopy technique enables us to determine the values of various parameters such as peak-to-peak line width ($\Delta H_{PP}$), Lande’s splitting factor (g-value), spin concentration ($N_s$) of Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ nanoparticles. The EPR spectra of the synthesized samples were recorded by scanning the magnetic induction at constant microwave frequency (i.e. 9.36 GHz in X-band EPR spectrometer) in the 4000 ± 4000 G scan region at 1.25×10$^2$ gain and 1×1 modulation at room temperature and is shown in Fig. 5. All the spectra were analysed using Lorentzian distribution function to obtain the values of various parameters such as g-value, line width, spin concentration and relaxation time and the values are listed in Table 2. The g-value is a constant of proportionality between the frequency and the field, is a function of the molecular motion, the paramagnetic properties and the symmetry of ions is calculated by the relation

$$g = \frac{h \nu}{\beta H}$$  (4)

Where, h is the Plank constant, $\nu$ is the microwave frequency $\beta$ is Bohr magneton and $H$ is the magnetic field at the resonance. The EPR spectra of these samples show a single broad signal with a very weak hump signal, indicating the presence of isolated Fe$^{3+}$, Ni$^{2+}$ and Zn$^{2+}$ ions of g-value about 3.4 [24]. The broadness of the EPR resonance signal is due to random orientation of ferromagnetic

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**Table 1:** XRD pattern analysis of Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ (0 ≤ $x$ ≤ 0.6) samples

<table>
<thead>
<tr>
<th>Lattice parameter (Å)</th>
<th>Crystallite size (nm)</th>
<th>Strain</th>
<th>X-ray density (gm/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{0.0}$Zn$</em>{1.0}$Fe$_2$O$_4$</td>
<td>8.368</td>
<td>10</td>
<td>0.00351</td>
</tr>
<tr>
<td>Ni$<em>{0.2}$Zn$</em>{0.8}$Fe$_2$O$_4$</td>
<td>8.331</td>
<td>12</td>
<td>0.00349</td>
</tr>
<tr>
<td>Ni$<em>{0.4}$Zn$</em>{0.6}$Fe$_2$O$_4$</td>
<td>8.287</td>
<td>16</td>
<td>0.00241</td>
</tr>
<tr>
<td>Ni$<em>{0.6}$Zn$</em>{0.4}$Fe$_2$O$_4$</td>
<td>8.264</td>
<td>17</td>
<td>0.00213</td>
</tr>
</tbody>
</table>

**Table 2:** EPR spectroscopy data analysis for Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ (0 ≤ $x$ ≤ 0.6) nanoparticles

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\Delta H_{PP}$ (Gauss)</th>
<th>g-value</th>
<th>$N_s$ (spin/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{0.0}$Zn$</em>{1.0}$Fe$_2$O$_4$</td>
<td>978.21</td>
<td>2.2820</td>
<td>2.7730 x 10$^{20}$</td>
</tr>
<tr>
<td>Ni$<em>{0.2}$Zn$</em>{0.8}$Fe$_2$O$_4$</td>
<td>999.58</td>
<td>2.1298</td>
<td>2.8141 x 10$^{20}$</td>
</tr>
<tr>
<td>Ni$<em>{0.4}$Zn$</em>{0.6}$Fe$_2$O$_4$</td>
<td>1070.55</td>
<td>1.9559</td>
<td>3.6442 x 10$^{20}$</td>
</tr>
<tr>
<td>Ni$<em>{0.6}$Zn$</em>{0.4}$Fe$_2$O$_4$</td>
<td>1172.44</td>
<td>1.9968</td>
<td>1.7787 x 10$^{20}$</td>
</tr>
</tbody>
</table>

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**Figure 4.** Magnetization curve for Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ samples (a) $x = 0.0$, (b) = 0.2, (c) $x = 0.4$

**Figure 5.** EPR spectroscopy measurement for Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ ($x$=0.0, 0.2, 0.4, 0.6) ferrite nanoparticle. (a) $x = 0.0$ (b) $x = 0.2$ (c) $x = 0.4$ and $x = 0.6$ nanoparticles.
particles in low nickel content sample, which scatter in directions of the anisotropic field of the nanoparticles [25]. It is found that peak-to-peak amplitude, point of minimum derivative and the point of maximum derivative shifting toward the lower field with increase in nickel content. The spin concentration is calculated by the comparison method where DPPH (2, 2-diphenylpicrylhydrazyl) is used as a standard reference material [25]. Spin concentration increases with nickel ion concentration up to x= 0.4 and then decreases for x=0.6 sample. This indicates the strong super-exchange interactions among the cations through oxygen ions present in Ni_{0.6}Zn_{0.4}Fe_{2}O_{4} nanoparticles. The peak to peak line width increases with the increase in nickel ion concentration. This variation is possible only by the strengthening dipolar interaction among cations through oxygen.

CONCLUSION

Nano-crystalline Ni_{x}Zn_{1-x}Fe_{2}O_{4} (x = 0, 0.2, 0.4, and 0.6) ferrites have been synthesized successfully by sol-gel method. The X-ray diffraction patterns confirm the single crystalline phase of Ni_{x}Zn_{1-x}Fe_{2}O_{4} ferrite nanoparticles. Lattice parameter decreases with the increase in nickel content, resulting in reduction in lattice strain. On the other hand, crystallite size increases with the increase in nickel content. Further, the saturation magnetization increases with nickel ion concentration. The properties of Ni-Zn ferrites can be effectively tailored by changing the composition parameters. The properties of the Ni-Zn ferrites can be effectively tailored by changing the composition parameters.

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REFERENCES

[1]. C-Y Hong et al., Ordered structures in Fe_{3}O_{4} kerosene-based ferrofluids, J. Appl. Phys. 81, 4275 (1997).
[16]. P. Kumar et al., Bandgap tuning in highly c axis oriented Zn_{1-x}Mg_{x}O thin films, Appl. Phys. Lett. 102, 221903 (2013).
[24]. L. Ki et al., Microstructural evolution and magnetic properties of NiFe_{2}O_{4} nanocrystals dispersed in amorphous silica, Chem. Mater. 12, 3705 (2000).

BIography

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