CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF Ni_{1-X}Mn_{X}Fe_{2}O_{4} NANOMATERIALS

3.1 INTRODUCTION

Chemically synthesized magnetic nanoparticles have drawn a lot of attention due to the unique magnetic properties derived from their nanosizes and uniform size distribution (Li and Sun 2000). The extremely small dimension of the nanostructured materials, this is responsible for their superior magnetic, dielectric and mechanical properties of these nonstructural materials compared to their conventional coarse-grained counterparts (Skandan 1994). The recent progress on the research and development of small size devices and systems are due to the advent of nanostructures. The synthesis of monodispersed magnetic nanoparticles has been an interesting area of study because of their wide spread applications such as magnetic recording, storage devices, transformer core and drug delivery (McMichael 1992, Ghasemi 2006b).

Ferrites are a group of technologically important materials having spinel (AB_{2}O_{4}) structures, which hold a very wide diversity of compositions and properties, and lead to applications such as fabrication of magnetic, electronic and microwave devices (Pannaparayil 1988). Nickel ferrite is one of the most versatile magnetic materials, which finds many applications both in low and high frequency devices (Abdeen 1998, Arshak et al 2001). The technological applications of nickel ferrites are microwave devices, power
transformers, rod antennas, read/write heads for high speed digital tape, etc., due to their low dielectric loss, mechanical hardness, high Curie temperature, resistivity and chemical stability (Sattar et al 2005, Mahmud et al 2006 and Son et al 2003). The type of “A” and “B” cations and their distribution between two interstitial sites in spinel ferrites can be tuned resulting in many interesting magnetic properties (Lakshman et al 2004).

Many synthesis approaches have been employed to prepare nanosized spinel ferrite materials, which include ceramic technique (Lezhong 2007), co-precipitation (Bonini et al 2004), micro emulsion (Wang and Kung 2004), micelle and hydrothermal methods (Liu 2004) and sol-gel process (Chander 2004). The metal alkaoxides having the valence greater than four explores the interesting physical and chemical properties. Recent studies has also proved the substitution of Manganese ions on the decrease of particle size due to cation distribution in a spinel lattice and are used in magnetic recording and electrical devices (Zhou et al 2002, Zhao 2006). A very limited number of reports are available for Ni$_{1-x}$Mn$_x$Fe$_2$O$_4$ synthesized by sol-gel combustion technique. The aim of the present investigation is to prepare highly dispersed and high quality Mn substituted Ni ferrite with a low sintering temperature involving less energy and low cost metal nitrates as raw materials and characterize them for electric, electrical and in catalytic properties.

3.2 EXPERIMENTAL TECHNIQUES
3.2.1 Nanoparticle Synthesis Ni$_{1-x}$Mn$_x$Fe$_2$O$_4$ nanoparticles

The Ni$_{1-x}$Mn$_x$Fe$_2$O$_4$ nanoparticles were synthesised by using the nickel nitrate, manganese nitrate, ferric nitrate, citric acid and polyvinyl alcohol by sol–gel combustion technique (Shobana et al 2007). The chemicals used in the present investigation were of analytical grade (AR) with high
purity of 99.99%. High purity double distilled water has been used in the course of preparation of samples.

The grained and annealed powders were characterized by powder X-ray diffraction (XRD) using (Philips1710, USA) X-ray diffractometer with CuKα as the radiation (1.5406 Å) source. Morphological and microstructural characterization of the ferrites was carried out by employing an Atomic Force Microscope (Digital Nanoscope II, USA). The powdered samples were fixed using acetone on a glass plate (2x2 mm). It was air dried for 30 min and used for AFM studies. Fourier transform infrared spectroscopic study was carried out in KBr medium using FTIR spectrometer (Shimadzu, FTIR-8400) in the range from 400 to 4000 cm⁻¹ with a resolution of 1 to 5 cm⁻¹. Thermal decomposition of the samples were studied from room temperature to 1000°C with heating rates from 10°C/min using a thermogravimeter (Perkin Elmer Analyzer). Magnetic measurements were carried out at room temperature using vibrating sample magnetometer (VSM) with a maximum field of 8000 Oe. The samples were weighed and covered with plastic tube and kept in the sample holder with help of a teflon tape. Mössbauer spectra were recorded using a conventional Mössbauer spectrometer (MS-500) of the electro-mechanical type, with 30 mCi57Co as a source in an Rh matrix at room temperature.

3.3 RESULTS AND DISCUSSIONS
3.3.1 Phase Analysis and particle size of powders

In order to confirm the phase formation of Ni₁₋ₓMnxFe₂O₄ nanoparticles, XRD studies have been carried out for all the prepared samples. The observed XRD patterns of the Ni₀.₂₅Mn₀.₇₅Fe₂O₄ sample NMF₁ and the samples calcinated at different temperatures 500°C, 700°C and 900°C (NMF₂, NMF₂ and NMF₃) are shown in Figure 3.1. The measured particle
size of all the samples is given in Table 3.1. The observed peaks in the spectra indicate pure single crystalline phase of spinel ferrite and no other extra reflections are observed (Figure 3.1). This is due to the existence of thermally formed single phase nanocrystalline ferrites. The observed peak positions in the present investigation agree well with the reported values. The lattice parameters were computed using d values of the six identified prominent corresponding to the (hkl) planes (220), (311), (222), (400), (511) and (440) values respectively. The determined lattice parameters confirm that the nanocrystalline ferrite samples are in cubic spinel structure (8.372Å). The crystallite formed is in a single phase indicating that the NiMn ferrites are directly formed after the auto combustion of gels. This is due to the heat generated from the exothermic reactions of nitrate and fuel (Arulmurugan et al 2006). The formation of single phase indicates the absence of any other impure phase in the ferrites and is a similar result as that as reported by George et al (2006) and Zhou et al (2006).

A sharp increase in the crystalline nature of the ferrite has been observed with increase in firing temperature for all samples. The same is evident from the observed results (Figure 3.1) and agrees well with the earlier report by Mozaffari et al (2003). The broad nature of peaks indicate that the particles are in nano range suggesting that the combustion has accelerated rapidly forward once it is ignited (Yue et al 1999). The crystalline size of the ferrites are obtained from the observed X-ray (220), (311), (222), (400), (511) and (440) diffraction peaks using Scherrer’s formula (Cullity 1972, Wu et al 2006),

\[ D = \frac{K\lambda}{\beta \cos \theta} \] (3.1)
where $\beta$ is the full width half maximum (rad), $\lambda$ the wavelength of the X-ray, 
$\theta$ the angle between the incident and diffracted beams (degree) and $D$ the particle size of the sample (nm). The estimated particle size of all the samples are given in Table 3.1. Figure 3.2 shows the variation of particle size as a function of temperature and it is inferred that the size of the particle increases with increase of temperature.

Table 3.1  Particle size of nanoparticles as a function of calcination temperature for $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ nanoparticles

<table>
<thead>
<tr>
<th>Temperature $^\circ\text{C}$</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{Ni}<em>{0.75}\text{Mn}</em>{0.25}\text{Fe}_2\text{O}_4$</td>
</tr>
<tr>
<td>300</td>
<td>27 (NMF$_1$)</td>
</tr>
<tr>
<td>500</td>
<td>56 (NMF$_2$)</td>
</tr>
<tr>
<td>700</td>
<td>78 (NMF$_3$)</td>
</tr>
<tr>
<td>900</td>
<td>104 (NMF$_4$)</td>
</tr>
</tbody>
</table>

Figure 3.3 illustrates the XRD patterns of the ferrites with different manganese (Mn) concentrations. The peaks in the spectra indicate that nanocrystalline $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ferrites and in the spinel structure and there are no other extra reflections. The particle size of the samples are 27, 19, 15 nm for $x = 0.25$, $x = 0.5$ and $x = 0.75$ of manganese, respectively, and were calculated by the Scherrer formula discussed above (Cullity 1978). It is evident that the particle size has decreased with the increasing concentration of Mn. Figures 3.4a and 3.4b show the variation of intensity with respect to manganese content at different (hkl) values (Figures 3.4a and 3.4b). The
variation of intensity of first two intense peaks ((311) and (440) plane) is due to the increase of Mn concentration. Further, it is inferred that the peak intensity has also been slightly shifted towards higher angles as the Mn content increases (Figure 3.4a, b).

The obtained particle size of the ferrite phase from the XRD studies is consistent with the particle size determined by AFM. This confirms that the citric acid is an effective burning agent for producing fine ferrite powder with sol-gel auto combustion method (Kim et al and Koh 2003, Hegde et al 1997). Further, homogeneity of the chemical composition of the ferrite particles has been acquired by thermal decomposition of nitrates. This type of single phase ferrite nanoparticles has been widely used for diverse applications.
Figure 3.1  XRD-Pattern of Ni$_{0.25}$Mn$_{0.75}$Fe$_2$O$_4$ nanoparticles at different calcination temperatures (a) 300°C, (b) 500°C, (c) 700°C and (d) 900°C
Figure 3.2   Particle size of Ni$_{1.3}$Mn$_{x}$Fe$_2$O$_4$ (x = 0.25, x = 0.5 and x = 0.75) as a function of temperature
Figure 3.3  XRD pattern of Ni$_{1-x}$Mn$_x$Fe$_2$O$_4$ ($x = 0.25$, $x = 0.5$ and $x = 0.75$) as a function of Manganese concentration
Figure 3.4 Variation of XRD intensity with respect to manganese concentration for (a) (311) plane and (b) (440) plane
3.3.2 Particle size and Morphological Analysis

From Figure 3.5a and Figure 3.5b, it is evident from the AFM images that for the samples NMF$_1$ and NMF$_4$ heated at 300°C and 900°C respectively confirm the cubic morphology of the particles. During the formation of nanoferrites, the gel boils first, results in a release of lot of gases. Because of the surface tension of the organic substances, the gel like soap bubbles blow up. The thermal effect leads to the weakening of the metal complex bond when the metal ions are pushed into the bubble surface. The expansion of gas ruptures the surface tension, once it reaches the ignition point of the combustible substances in the gel. Thus, the gel burns automatically and violently. The sudden combustion causes the gathering of organic complex together and accelerates the solid- solid reaction resulting in the formation of a lot of nanoparticles at a lower firing temperature (Kingery and Uhlmann 1976).

It is inferred that an increase in calcination temperature increases the particle size. The nanostructure prepared by this nature is preferred for reducing the media noise and increasing the storage density in the magneto-optical recording applications (Ponpandian et al 2002). Figure 3.5b shows the existence of agglomeration of the NiMn ferrite nanoparticles. This may be due to evaporation of polymer at high temperature. In order to confirm the particle size of the Ni$_{1-x}$Mn$_x$Fe$_2$O$_4$ samples, transmission electron microscopy measurement were carried out (Figure 3.6). The results are consistent with XRD results discussed in section 3.3.1. The composition of the prepared samples measured by EDX is also in expected ratio.
Figure 3.5  Topographic view of Ni$_{0.25}$Mn$_{0.75}$Fe$_2$O$_4$ nanoparticles  
(a) 300°C and (b) 900°C
Figure 3.6  Topographic view of Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ nanoparticles (a) samples at 300°C and (b) samples at 900°C (c) diffraction pattern at 300°C
3.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 3.7 shows the IR spectra of as prepared samples at 300°C. The FTIR bands are sharp, and are characteristic of the evidence, for the formation of ferrite. The bands observed around 3430.21 cm\(^{-1}\) and 1521.69 cm\(^{-1}\) frequencies are ascribed due to the stretching modes and H-O-H bending vibration of the free or absorbed water molecules. The band at 580 and 680 cm\(^{-1}\) are the characteristics of Ni ferrites as reported elsewhere (Wu et al 2004). Anti-symmetric NO\(_3\)-stretching vibration directly arises from the residual nitrate groups in the xerogel. The peak observed at 770 cm\(^{-1}\) may be due to the oxide lattice deformation.

A clear observation of the range of bands in the regions between 1410 and 1260 cm\(^{-1}\), 1150 and 1410 cm\(^{-1}\), 1380 and 1350 cm\(^{-1}\), 1450 and 1410 cm\(^{-1}\) and 470 and 430 cm\(^{-1}\) are respectively due to the O=H bending, C-O stretching, nitrate ions, CH\(_3\) and CH\(_2\) groups respectively as reported in ferrite (Sindhu et al 2006, Willard and Merrit 1995). The peak around 574.73 cm\(^{-1}\) confirms the presence of uniformly distributed ferrite particles, which supports the observation made from the XRD results in the present investigation.

3.3.4 Thermal studies

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) analyses of the precursor were carried out from 40° to 1020°C (Figure 3.8). Generally, thermal degradation of dried nitrate-citrate consists of 3 steps namely dehydration, decomposition of citrate to carbonate and formation of ferrite. It indicates that there is only one step weight loss below 900°C. The corresponding relative mass loss is about 0.02% within 100°C. Planar water is volatalized first and corresponds to small mass loss.
Figure 3.7 FTIR spectra of Ni$_{1-x}$Mn$_x$Fe$_2$O$_4$ (x = 0.25, x = 0.5 and x = 0.75) nanoparticles (a) 300°C for x = 0.25, (b) 500°C for x = 0.25, (c) 300°C for x = 0.5, (d) 500°C for x = 0.5, (e) 300°C for x = 0.75 and 500°C for x = 0.75)
(Yu et al 2006). Following this, a prominent mass gain of 0.05% is obtained at 700°C. It may be due to the interaction of capped nanomaterials with oxygen at higher temperatures and indicates the enhancement of ferrite formation (Hegde et al 1997). DTA was studied to analyze the existence of ferrite and it confirms that the thermal decomposition of metal nitrates was perfectly in ferrite phase. Two broad exothermic peaks appear at about 230°C and 400°C respectively. The exothermic peak around 230°C may be caused by the reaction of nitrates with citric acid whereas the exothermic peak at 400°C corresponds to the decomposition of citric acid (Yue et al 1999). A narrow exothermic was centered at 973.29°C and marks the completion of reaction.

The TGA and DTA thermogram of the sample decomposed in N₂ atmosphere are shown in Figure 3.8b. They reveal that major part of the weight loss (12%) occurs below 200°C. There is an endothermic peak around 50°C in the DTA curve. It mainly corresponds to the evaporation of residual free water (Yu et al 2006). There is a slow mass loss in the temperature range from 200°C-600°C and the relative mass loss is about 2.7%. On its DTA curve, there is a broad exothermic peak centered at 300°C and 520°C (Figure 3.8b). These phenomena imply the formation of different phases as a result of solid to solid interaction between the corresponding oxides (Yu et al 2006). The possible remains above 200°C might be iron oxides, goethite, lepidocrocite, nickelous oxide, manganese oxide and a few organic giblets (Hegde et al 1997). An endothermic peak at 590°C (Figure 3.8b) is due to the thermally induced anionic oxidation-reduction reaction of the gel. Here, citrate ion acts as a reductant and nitrate ions act as an oxidant (Wu et al 2004).

Figure 3.8c shows the TGA-DTA of ferrite particles with \( x = 0.75 \) of Manganese. The mass losses are found to be at temperatures around 100°C,
250°C, 680°C and 800°C. The observed weight loss at 150°C is attributed to the loss of physical or chemical desorption of water, while the loss above 250°C is due to the decomposition of capped organic molecules as reported earlier reports (Ponpandian et al 2002, Lázár et al 2002). A weight gain is also observed at 450°C which results an endothermic peak around 450°C in DTA curve. This may be due to the reaction,

\[
2\text{Fe}_3\text{O}_4 + \frac{1}{2} \text{O}_2 \rightarrow 3\text{Fe}_2\text{O}_3.
\]

Finally, there is another exothermic peak at 800°C which confirms the completion of ferritization. All of the observed results reveal that the substitution of Mn reduces the ferritization process as follows: For the Mn concentrations \(x = 0.25\), \(x = 0.5\), and \(x = 0.75\), the temperatures of ferritization are respectively, \(973.29^\circ\text{C}\), \(927.81^\circ\text{C}\) and \(898.45^\circ\text{C}\). This may be reduction of temperature of ferritization attributed to the decreasing particle size which occurs due to the substitution of Mn of ionic radius (0.80 Å) with \(\text{NiFe}_2\text{O}_4\) (Zhou et al 2002). The observed narrow endothermic peaks confirm the crystallization of nanoferrites. Exothermic peaks were observed around 800 to 900°C (Figure 3.8c) of \(\text{NiMn}\) ferrites. The absence of further exothermic peaks suggests that the ferritisation is completed. All the peaks are much lower than that at 1300°C confirms and the association with Ni ferrite produced by conventional method (Sindhu et al 2006).
Figure 3.8  TGA-DTA Pattern of Ni$_{1-x}$Mn$_x$Fe$_2$O$_4$ nanoparticles (a) TGA-DTA for $x = 0.25$, (b) TGA-DTA for $x = 0.5$ and (c) TGA-DTA for $x = 0.75$
3.3.5 Magnetic studies

3.3.5.1 Hysteresis loop

Magnetic characterization of the $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ particles was carried out using vibrating sample magnetometer (VSM) at room temperature upto a maximum field of 8 K Oe. The magnetic parameters (Saturation magnetization ($M_s$) and Coercivity ($H_c$)) obtained by hysteresis curves are illustrated in Figures 3.9 and 3.10. When the particle size is reduced to the critical size of single-domain, the coercivity is decided by magnetic domain rotation, so the coercivity reaches maximum. The magnetic domain increases with the increase of thermal treatment and so the particle size grows for all the samples. The observed results reveal that saturation magnetization value decreases with decrease of particle size. The observed results agree well with previous reports (Cullity 1972, Silva 2004). The coercivity of the sample increases with calcination temperature, sometime it shows a maximum close to highest calcination temperature and then decreases (Mazz et al 2007).

![Figure 3.9 Saturation magnetization values of $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ (x = 0.25, x = 0.5 and x = 0.75) as a function of calcination temperature](image-url)
Figure 3.10 Coercivity values of $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0.25$, $x = 0.5$ and $x = 0.75$) as a function of calcination temperature

Variation of hysteresis loop has been obtained with the variation of the Mn content (Figure 3.11). Figure 3.11 shows that the Ms value of all samples increase with an increase in crystallite sizes. Ms decreased rapidly with the Mn content in ferrite. For the same calcination temperature, the Ms value of the samples doped with Mn$^{2+}$ ions are less than that of undoped one. This may be due to smaller crystallite sizes under the influence of Mn$^{2+}$ in sub-lattice. Figure 3.12a,b depicts the variation saturation magnetization (Ms) and coercivity (Hc) as function of manganese concentration. The magnetization (Ms) is observed to vary with Mn content as follows: Ms (for Mn $x=0.25$) > Ms (for Mn $x=0.5$) > Ms (for Mn $x=0.75$). Also the change in Ms is closely related to the variation of the crystallite size which is influenced by the increasing manganese concentration ($x$).
Figure 3.11  Hysteresis loop of Ni$_{1-x}$Mn$_x$Fe$_2$O$_4$ nanoparticles with different Mn concentration (x=0.25, x=0.5 and x=0.75)
Figure 3.12 (a) Variation saturation magnetization as a function of Mn and (b) Variation coercivity as a function of Mn
On the other hand, the Hc is found to decrease with increasing x. The decrease of Hc is due to the decrease of Ni$^{2+}$ content (x) on the B–sites which would have migrated to A-sites. It may be due to the distribution of divalent cations (Mn$^{2+}$) in the spinel lattice by a small number in the midst of Mn$^{3+}$ ions in B sites resulting in larger B-sublattice magnetic contribution to the magnetization. Further increase in doping of Mn decreases the strength of the exchange interactions, and therefore saturation magnetization value decreased. All of these observed results also agree well with the earlier reports (Zhou et al 2002, Caltun 2007).

### 3.3.5.2 Mössbauer spectra

The Mössbauer spectra of NiMn ferrites nanoparticles recorded at room temperature are shown in Figure 3.1. The parameters such as quadrupole splitting, hyperfine field and isomer shift obtained from Mössbauer spectra are given in Table 3.2. The observed results indicate that the quadrupole splitting of the system is very small. Therefore, there is no distribution of A and B sites. The first order quadrupole splitting are averaged to zero, which is one of the characteristics of the spinel ferrites. From the Mössbauer spectra, the average values of the hyperfine field (BHF) for the sample NMF$_1$ are 48.74 and 45.65 Tesla, for sample NMF$_2$ are 49.445 and 46.44 Tesla, and similarly for sample NMF$_4$ are 50.77 and 48.09 Tesla. Further, the observed chemical isomer shift values are almost same as those of Mn ferrites (Bhat et al 1989, Pollard 1988). The values of quadrupole splitting for all samples have been found to be negligibly small indicating the presence of cubic point symmetry at both sites (Puri et al 1989).
Figure 3.13 Mössbauer Spectra of Ni$_{1-x}$Mn$_x$Fe$_2$O$_4$ nanoparticles at room temperature.
Table 3.2  Mössbauer hyperfine parameters at room temperature for \( \text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4 \) nanoparticles

<table>
<thead>
<tr>
<th>Sample</th>
<th>Isomer Shift (mm/s)</th>
<th>Q. Splitting (mm/s)</th>
<th>BHF (Tesla)</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMF(_1)</td>
<td>0.321 ±0.006 0.371±0.012</td>
<td>0.012±0.011 -0.009±0.025</td>
<td>48.74±0.05 45.65±0.113</td>
<td>67.77 32.23</td>
</tr>
<tr>
<td>NMF(_2)</td>
<td>0.318 ±0.009 0.322±0.030</td>
<td>0.010±0.018 0.014±0.057</td>
<td>49.25±0.104 46.44±0.299</td>
<td>74.20 25.80</td>
</tr>
<tr>
<td>NMF(_4)</td>
<td>0.348 ±0.010 0.309±0.013</td>
<td>-0.093±0.020 0.024±0.029</td>
<td>50.77±0.072 48.09±0.102</td>
<td>54.43 45.57</td>
</tr>
</tbody>
</table>

3.4 CONCLUSIONS

The \( \text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4 \) nanoparticles have been prepared using sol-gel combustion technique. An ample range of nanosize particles has been obtained using polyvinyl alcohol as a capping agent. The size of the particles and morphology of the ferrites have been confirmed through XRD, TEM and AFM studies. The observed peaks in FTIR spectra confirm the presence of functional groups, while ionic distribution and the phase identification have been carried out from the Mössbauer spectra. The percentages of weight loss and gain have been obtained at different temperatures employing the thermal properties of \( \text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4 \) nanoparticles. From TGA-DTA studies, it is found that ferritization temperature decreases with increasing Mn concentration (\( T_{\text{Fe}} \) for Mn (0.25) = 973.29°C, \( T_{\text{Fe}} \) for Mn (0.5) = 927.81°C and \( T_{\text{Fe}} \) for Mn (0.75) = 898.45°C). The magnetic coercivity increases with calcination temperature initially due to thermally activated surface and interfacial defects and then decreases for further increase in calcination temperature and this can be attributed to the growth of magnetic domains with the increase of grain size. The present study thus reveals that sol-gel combustion technique was found to be one of the simplest effective chemical routes for preparing wide range of nanoparticles for diverse applications.