

Synthesis and Characterization of Mixed Ferrites

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Abstract- In this work we prepare nanocrystalline mixed ferrites by equilibrated low entropy routes with generic formula of $Mn_xNi_{1-x}Fe_2O_4$. Two series of samples have been prepared where "x" varies as 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 the samples have been prepared by chemical co-precipitation route. For the first calculated amount of salts of Mn, Fe and Ni were dissolved in deionized water and stirred for a few minutes. 0.1 M NH_4OH solution was then slowly added drop-wise under vigorous stirring. The alkali addition was continued till the pH of the solution was 10 and was left undisturbed for 1hour for complete digestion. The precipitate was then washed thoroughly till pH 7 and then heated to 600 °C. For the next series "x" was kept fixed at 0.5 and the same synthesis steps were repeated. The sample was divided into three batches and heat treatment was performed at 600 °C, 900 °C. The samples were checked for their phase purity by x ray diffraction which confirmed the spinel phase without any impurity. Dielectric measurements were performed within a frequency window of 1 Hz to 1 MHz the dielectric dispersion can be well explained by Koops and Maxwell – Wagner theory. Raman spectroscopy also gave detailed information about the structural order of the samples.

Index Terms- Nanocrystalline, spinel structure, chemical coprecipitation, Raman spectroscopy, XRD (x-ray diffraction), JCPDS (joint committee for powder diffraction standards)

I. INTRODUCTION

Ferrites are mixed metal oxides with iron (III) oxide as main component it is a magnetic material exhibit in ferrimagnetic ordering and magnetism due to the super exchange interaction [1]. Present day's nanocryastalline mixed spinel structure ferrites are the particular research topic for the researcher all over the world, because of large variety of unique results associated with electric, dielectric, magnetic properties. $Mn_xNi_{1-x}Fe_2O_4$ manganese nickel ferrite belongs to the class of mixed spinel ferrite where "x" varies from 0.0 to 0.5 (variation of cation) shows unexpected properties at nano regime due to the re-distribution of cations, cation ionic radii, crystal field effect, presence of ion to specific site, ionic charge are the main factors that causes distribution of cation in mixed spinel ferrites [2]. Spinel ferrites structures partially determine by oxygen ion in a cubic arrangement there are two types of interstitial spaces between the anion tetrahedral co-ordinate site and octahedral co-ordinate site [1]. For the satisfactory results of cation distribution in tetrahedral and octahedral sites we prepare the series of sample varying the no. of cations and studied through Raman

spectroscopy .Electrical properties of samples were studied by dielectric studies and porosity of the samples derived from x-ray densities which utilizes structural parameters obtained through XRD measurement. The nanocrystalline mixed spinel ferrites materials used in various technological issues like nano ferrite doped microstrip patch antenna for improved the overall antenna performance, microwave dielectric property study and antenna miniaturization [3,4] .Application of nano ferrites are in fashion these days because of its simple preparation, compatibility with electrical circuits, low overall cost and light weight these have numerous application in almost every field some of them like medical, electric, power, communication, mechanical etc.

II. EXPERIMENTAL

The nanocrystalline mixed ferrite material of manganese nickel ferrite of formula $Mn_xNi_{1-x}Fe_2O_4$ prepared by chemical co-precipitation method, Solution of $MnCl_2 \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ with distilled water is prepared The main solution of $Ni^{2+}, Fe^{3+}, Mn^{2+}$ were Mixed according to the calculated weight of samples. Calculated amount of salt of Mn, Fe, and Ni were dissolved in deionized water and stirred for a few minutes. 0.1M NH_4OH solution was then slowly added drop-wise under vigorous stirring the alkali addition was continued till pH of the solution was 10 and was left undisturbed for 1 hour for complete digestion. The reactions involved are

- $MnCl_2 + 2NH_4OH \rightarrow Fe(OH)_3 + 2NH_4NO_3$
 $Mn(OH)_2 \xrightarrow{Heat} MnO + H_2O$
- $Ni(NO_3)_3 + 2NH_4OH \rightarrow Ni(OH)_3 + 2NH_4NO_3$
 $Ni(OH)_2 \xrightarrow{Heat} NiO + H_2O$
- $Fe(NO_3)_3 + 3NH_4OH \rightarrow Fe(OH)_3 + H_4NO_3$
 $2Fe(OH)_2 \xrightarrow{Heat} Fe_2O_3 + H_2O$

After calculation we have Fe, Ni, Mn in 250 ml for 0.04M is 0.7985gm, 0.7469gm, 0.7093gm respectively. After chemical co-precipitation process we separate nanoparticles formed in the bottom of beaker from supernatant by centrifuge machine operating at a speed of 2200 rpm and duration is fixed at 4 or 5 minutes, the centrifugal process is continued till the pH reached at 7 after this we done the centrifugal process with alcohol we repeat this process at least 2 times with alcohol and then obtained the final product but it is still in wet condition so left it for whole

day to dried it. By repeating whole process we prepare two series of samples in first series where “x” varies as 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 is heat treated at 600 °C for 8 hours and for second series where x=0.5 kept constant The sample was divided into three batches and heat treatment was performed at 300 °C, 600 °C, 900 °C for 8 hours respectively and finally we obtained our desired nanocrystalline manganese nickel ferrite material.

III. RESULTS AND DISCUSSION

3.1 XRD:

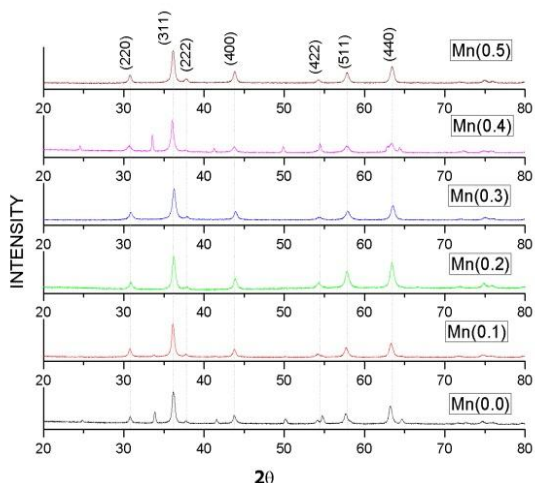


Fig1.1 XRD pattern of Mn_xNi_{1-x}Fe₂O₄, (Manganese Nickel Ferrite) where “x” varies as 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5.

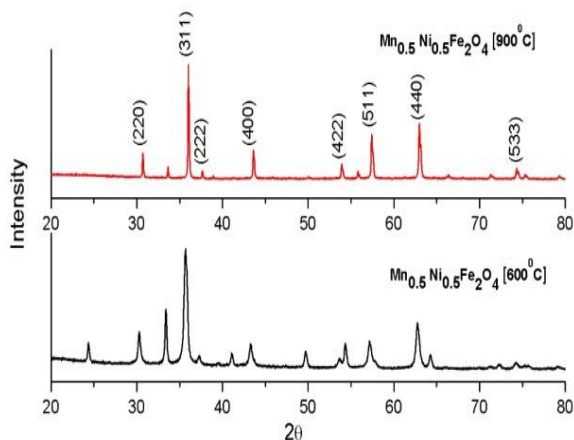


Fig1.2XRD pattern of Mn_{0.5}Ni_{0.5}Fe₂O₄, (Manganese Nickel Ferrite) at 600°C and 900 °c

The X-ray diffraction patterns of the synthesized ferrite nanocrystals have been shown in Fig 1.1 and 1.2

The peaks in XRD patterns illustrate the characteristic peaks of single phase cubic spinel structure. Peak intensity is indicative of high degree of crystallinity of prepared ferrites. The existence of the (220), (311), (222), (400), (422), (511) and (440) major lattice planes in the XRD patterns confirms the formation of spinel cubic structure with the Fd3m space group, which is consistent with the powder diffraction file of JCPDS. The patterns were compared with standard data (JCPDS PDF card

No. 074-2082) and the formation of single phase cubic MnNiFe₂O₄ nanoparticles in all the samples except x=0.1 and x=0.4 was confirmed. The mean particle sizes (D) were calculated from the X-ray line broadening of the (311) diffraction peak using the **Scherrer’s equation**:

$$D = k \lambda / \beta \cos\theta$$

Where D is the crystallite size, λ is the wavelength of X-ray radiation, θ is the Bragg angle and β is the full width at half maximum (FWHM). From the analysis of the XRD spectra we found that the mean particle diameter (D) is nearly the same for all synthesized specimens, ranging from 18- 22 nm which shown in table 3.1. Broad peaks indicating the fine grain size of the samples. With higher annealing temperature, powders have stable structure and fine crystallization, when the annealing temperature is increases Intensity of the peaks in all XRD spectra is increased and the sharpness of peaks indicated the highly crystalline nature of the precipitate. The results indicate that the crystalline sizes increase with the annealing temperature. The crystallite sizes of annealed powder increase from 21 to 51 nm with the annealing temperature increase from 600°C to 900°C. The reason why the grain sizes increase dramatically at annealing temperature of 900°C might be due to the dominance of the activation energy during the grain growth process [5]. At the higher temperature the removal of extra undefined phases also noticed.

Table 3.1– Average particle size estimated from the diffraction spectrum in Figure 1.1 by using FWHM.

SAMPLE NAME	2θ	FWHM (B) IN RADIANS	AVERAGE SIZE OF THE PARTICLE (NM APPROX.)
Mn _{0.0} Ni ₁ Fe ₂ O ₄	36.16	0.40	21
Mn _{0.1} Ni _{0.9} Fe ₂ O ₄	36.06	0.38	22
Mn _{0.2} Ni _{0.8} Fe ₂ O ₄	36.27	0.46	18
Mn _{0.3} Ni _{0.7} Fe ₂ O ₄	36.24	0.41	20
Mn _{0.4} Ni _{0.6} Fe ₂ O ₄	36.14	0.39	21
Mn _{0.5} Ni _{0.5} Fe ₂ O ₄	36.20	0.39	21

Table 3.2– Average particle size estimated from the diffraction spectrum in Figure 4.2at 600°C and 900°C by using FWHM.

Mn _{0.5} Ni _{0.5} Fe ₂ O ₄ [600°C]	36.20	0.39	21
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$Mn_{0.5}Ni_{0.5}Fe_2O_4$ [900°C]	36.05	0.17	51
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3.2 Dielectric study

The samples for dielectric measurement were pressed by applying a pressure of 120-150 Kg/cm² tones to get compact circular pellets with dimensions 12mm in diameter and approximately 0.5mm to 2 mm in thickness. The LCR meter is compactable with such dimension of the pellets. The dielectric constant measurements of the samples at low and high frequencies from a few Hz to 10MHz were carried out by a Alpha-A High Performance Modular Measurement System (NOVOCONTROL). The temperature variation studies are also carried out. The dielectric constant of the sample can be calculated using the equation,

$$\epsilon_r = (c d / \epsilon_0 A)$$

Where, A= area of sandwiched structure

c= Capacitance measured by LCR

d = Thickness,

ϵ_0 = Absolute permittivity

Koop's and Maxwell Wagner theory well explain the dielectric behavior of ferrites [6], the variation of Mn concentration on dielectric properties of mixed ferrites explain here,. fig (a) shows the dielectric permittivity decreases with the increase in frequency the reason behind of it is with the increase of Mn concentration decrease in Ni⁺² nickel ions concentration consequently the Fe⁺² ions results less no. of pairs for hole and electron hopping as a result charges getting build up across the grain boundaries and resistance increases, this may be the reason behind low permittivity value in Mn rich concentration. From fig.(b) it is observed that tanδ decreases with increase of frequency and at high frequency it is constant for all samples, dielectric relaxation occur in the frequency range of 100Hz to 1000Hz due to the hopping frequency of charge carriers equal to the applied field frequency[1]. It is seen that from fig. there is absence of relaxation in Mn rich concentration due to the unavailability of hopping charges, for manganese nickel ferrite conductivity and resistivity can be explain on the basis of hopping of electron and hole charges on the octahedral site fig (c) and fig (d).for the second series the fig (e) and fig (f) shows the changes in loss tangent and dielectric permittivity and it can explain as the temperature increases from 300 °C to 600 °C and 900 °C there is decrease in permittivity in great extent due to charges accumulation on grain boundaries.

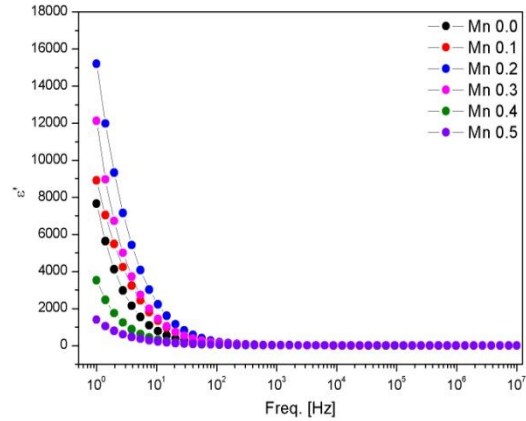


Fig (a): permittivity vs. frequency plot

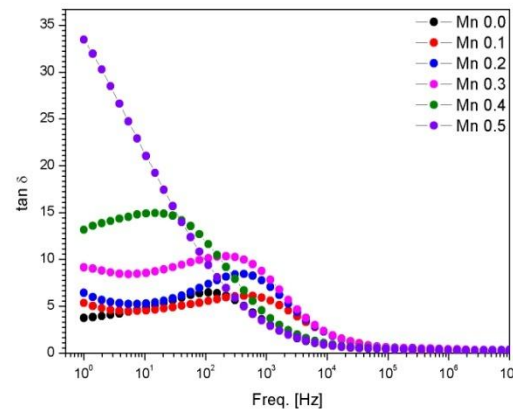


Fig (b): loss tangent vs. frequency plot

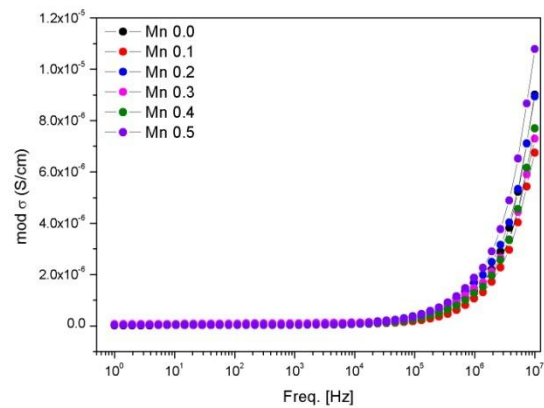


Fig (c): conductivity vs. frequency plot

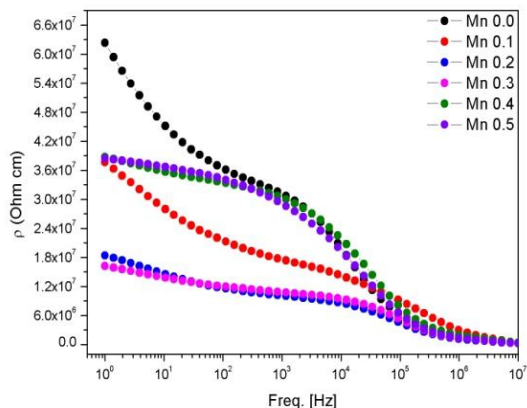


Fig (d): resistivity vs. frequency plot

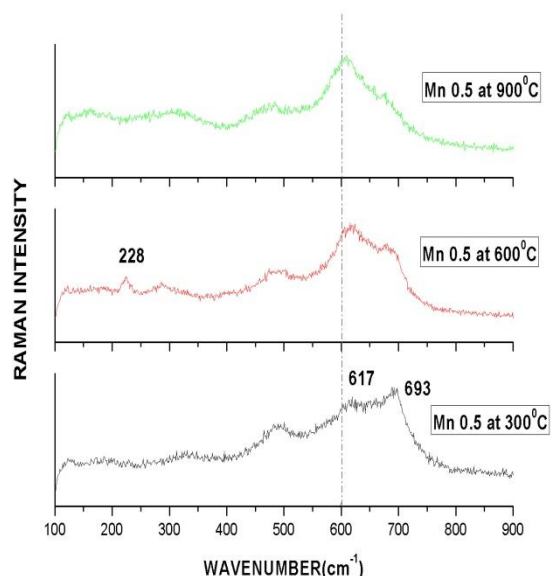


Fig.(h) Raman spectra for the second set of series

3.3 Raman Spectroscopy

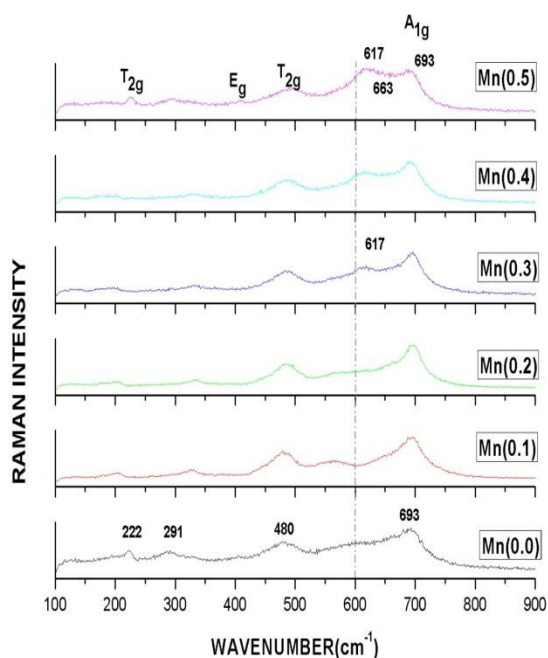


Fig.(g) Raman spectra for the first set of series

According to the literature five Raman active bands A_{1g} , E_g , and three T_{2g} [7]. Fig (g) shows the room temperature Raman spectra of $Mn_xNi_{1-x}Fe_2O_4$ sample where “x” varies from 0.0 to 0.5 observed in the range of 0-1500 cm^{-1} , the vibrational modes are around at 222 cm^{-1} , 291 cm^{-1} , 480 cm^{-1} , 693 cm^{-1} , since modes above 600 cm^{-1} corresponds to the tetrahedral sub lattice (A_{1g} symmetry) and due to the motion of the oxygen atoms in tetrahedral group and below refers octahedral sub lattice (T_{2g} symmetry) [8,9]. Broadening of modes in Raman spectra is due to the strain development and reduction in grain size [9,10] in Nano crystalline ferrites phonons with q (phonons) > 0 involves in scattering so that broadening and shift of Raman spectra observed. The mass difference between the three ions (Ni^{2+} , Fe^{3+} , Mn^{2+}) splits the A_{1g} mode in three different energy value the lightest ion Ni^{2+} responds to around 693 cm^{-1} for $x=0.3$ to 0.5 the heaviest one i.e. Fe^{3+} respond to around 617 cm^{-1} and an intermediate mode of Mn^{2+} ion around 663 cm^{-1} . On relative intensity and peak position can be explained considering alloy effects, resulting from the introduction of a new ion at increasing content. Further, the Raman frequency depends on the Fe(Ni)-O and bond length. The intensity of the highest wavelength Raman mode (initially around 693 cm^{-1}) decreases with increasing Mn-content the intensity of the Raman mode peaking around 617 cm^{-1} increase proportionally. Those with q (phonons) >0 take part in the Raman scattering process, resulting in the of the peak position and the broadening of the peak width. The Raman intensity of the signal increases as the sintering temperature is increased, as shown in figure (h) the intensity of Raman mode 617 cm^{-1} increases at 900 $^{\circ}C$ and mode 693 cm^{-1} is disappeared at 900 $^{\circ}C$ in fig (h) The shift toward lower wave number is attributed to the crystalline disorder and also to the presence of grain boundaries, which are large in small-sized nanomaterials. Another important parameter of Raman signal, i.e. the bandwidth, shows broadening for the small-sized nanomaterials (~20 nm), which also supports the crystalline disorder. The Raman shift toward lower wave number and the line broadening

are generally observed in polycrystalline materials and are attributed to the confinement of optical phonons in a small crystalline particle [11].

IV. CONCLUSION

Nanocrystalline manganese Nickel ferrite particles for $x=0$ to $x=0.5$ and europium and terbium doped Nickel ferrite for $x=0.02, 0.05, 0.1$ were prepared using wet chemical co-precipitation technique. The particles were found to be exhibiting a spinel structure with sizes varying from 21nm - 51nm. Overall result of xrd pattern confirms the spinel cubic structure with high degree of crystallinity of prepared ferrites. The result of Raman modes confirms the five Raman modes and distribution of cation distribution in octahedral and tetrahedral sub lattices in agreement with the as-synthesized samples. The frequency and temperature dependence of the dielectric parameters of. The mechanism of dielectric polarization was found to be similar to that of conduction process involving the hopping of charge carriers. The decrease in ϵ with Mn substitution point to the decrease in availability of Ni^{2+}/Ni^{3+} and Fe^{2+}/Fe^{3+} pairs with increasing Mn. The $\tan\delta$ and exhibit strong relaxation peaks and relaxation time (Γ) was estimated from these relaxations.

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