International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064, Impact Factor (2013): 4.438
www.ijsr.net

Structural and Electrical Conductivity Properties of Manganese Substituted Ni Nanoferrite Particles Prepared by Co-Precipitation Technique

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Abstract: ***Results of X-ray diffraction and D. C. Electrical Resistivity obtained on the series of $Mn_xNi_{1-x}Fe_2O_4$ (x=0.5, 0.6, 0.7) ferrite nanoparticles prepared by co-precipitation method and heat treated at 500°C are reported. Average crystallite size is estimated to be in the range of 5.4 nm – 15 nm . It is observed that crystallite size and lattice parameter increase with increase in Mn^{2+}concentration. The electrical conductivity increases with increase in Mn^{2+} concentration. At relatively low sintering temperatures, the samples exhibit superparamagnetism and complete ferrite phase was observed at higher heat treatment.***

Keywords: XRD, D. C. Conductivity, Ferrites, Nanoparticles, activation energy.

1. Introduction

The bulk properties of ferrites change as their dimensions are changed to scale. Some phenomena like superparamagnetism, spin canting, core-shell, cation distribution etc. have been observed in different nanoferrites. Mn-Ni Spinel ferrites are ceramic ferromagnetic materials which possess excellent magnetic and electrical properties useful for electromagnetic applications [1]. Many researchers are extensively studying Mn-Ni ferrites in nano form because their structural and magnetic properties can be altered depending upon composition, particle size and sintering temperature [2]. The method of preparation, composition and sintering temperature influence the formation of ferrite phase [3]. In Mn-Ni mixed ferrites, Ni^{2+}ions preferentially occupy B-sites and Mn^{2+} ions are randomly distributed between A and B sites. The cation distribution is influenced by the substitution level of metal ions in tetrahedral and octahedral sites which in turn influence the structural, magnetic and electrical properties of ferrites. In nanoregime, magnetic anisotropy energy KV is less than the thermal energy where V is volume of the particle and K is magnetic anisotropy constant. In this condition, the constituent particles exist as single domains (Ds) and are of randomly oriented like magnetic spins in paramagnetic state which is known as superparamagnetism. The condition for superparamagnetism is given by $KV \approx k_BT_B$. Where k_B is Boltzmann's constant and T_B is blocking temperature. The blocking temperature is defined as the temperature for which the relaxation time τ is equal to the characteristic time of the measurement technique. For critical size (Dc) nanoparticles, T_B is below the room temperature and superparamagnetism is observed even at room temperature [4].

In this paper the results obtained in the X-ray diffraction (XRD) and D.C. Conductivity of co-precipitated $Mn_xNi_{1-x}Fe_2O_4$(x=0.5, 0.6, 0.7) ferrite nanoparticles and heat treated at 500°C are presented.

2. Experimental

The mixed spinel ferrite $Mn_xNi_{1-x}Fe_2O_4$ (x = 0.5, 0.6, 0.7) have been synthesized by co-precipitation method. High purity Manganese Chloride ($MnCl_2$), Nickel chloride ($NiCl_26H_2O$), Ferric chloride ($FeCl_26H_2O$) are taken as starting materials. Each material was weighed separately and dissolved in a suitable quantity of de-ionized water to make 0.5M solutions. The cationic solutions were mixed thoroughly using a magnetic stirrer for complete dissolution and heated to 60°C. The NaOH solution of 0.4M concentration was prepared and heated to 60°C, and quickly transferred into the hot cationic solution, while maintaining the stirring and heating till complete precipitation occurs. Heating of the precipitate in its alkaline condition is continued for 1hour at soaking temperature of 100°C. Stirring is further continued for 12 hours for complete aging. The precipitated particles were washed several times and were dried at 80°C for 2days. The ferrite powders have been gently pressed under a pressure of 5 tons/cm^2 into pellets of uniform diameter of 1.5cm and varying thickness of 2 mm to 3 mm. The pellets were sintered at 500°C in air and ground into fine powder in agate mortar. The powder is used for XRD and electrical conductivity measurements.

3. Results and Discussion

3.1 XRD Studies

The X-ray diffractograms of $Mn_xNi_{1-x}Fe_2O_4$ (x = 0.5, 0.6, 0.7) sintered at 500°C in air are given in Fig.1 and the values of crystallite sizes and lattice parameter are given in Table.1.From XRD graphs, it was observed that at low concentration of Mn^{2+}, complete ferrite phase is not formed. But the ferrite phase increases with increase in Mn^{2+} concentration. It is further observed that some additional secondary peaks are also formed, the origin of which may be attributed to formation of α-Fe_2O_3.

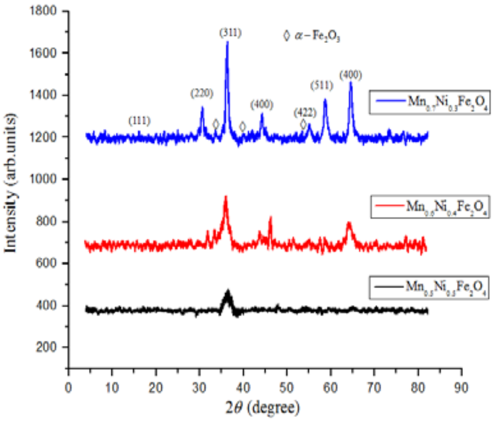

Figure 1: XRD patterns of $Mn_xNi_{1-x}Fe_2O_4$ (x= 0.5,0.6,0.7) nanocrystallineferrite samples sintered at 500°C. ◊ peaks are due to α – Fe_2O_3

Table 1: Crystallite sizes (D) and Lattice parameter (a)

Composition	D *(nm)*	*a* (Å)
$Mn_{0.5}Ni_{0.5}Fe_2O_4$	5.4	8.239
$Mn_{0.6}Ni_{0.4}Fe_2O_4$	7.2	8.269
$Mn_{0.7}Ni_{0.3}Fe_2O_4$4	15.0	8.312

However these peaks are absent in the samples sintered at higher temperatures. The peaks characterized by (111), (222), (311), (400), (422), (511) and (440) were due to spinel structure and match with those reported earlier [5]. It was observed that the crystallite size and the lattice parameter increase with increase in Mn^{2+} ion concentration. The linear increase in lattice parameter is attributed to the larger ionic radius of Mn^{2+} (0.82 Å) compared to that of Ni^{2+} (0.72 Å) [5].

3.2 D. C. Electrical Conductivity Studies:

The conductivity studies are useful to understand the transport mechanism of cations in nanocrystalline ferrites. In the present work, two- probe technique was used to measure the D.C. electrical resistivity of $Mn_xNi_{1-x}Fe_2O_4$ (x= 0.5, 0.6, 0.7) nanocrystalline ferrite samples sintered at 500°C over the temperature range of 303K - 423 K (30°C-150°C) and the graphs are presented in Fig.2. The calculated values of activation energies in ferrimagnetic region (E_f), paramagnetic region (E_p) and difference of activation energies (ΔE) are presented in table 2. The room temperature resistivity of $Mn_xNi_{1-x}Fe_2O_4$ (x = 0.5, 0.6, 0.7) nanoferrite system is found to be in the range of 3.55 x10^6 Ω-cm to 11.38x x10^6 Ω - cm. It was observed that as Mn^{2+} ion concentration is increased, the resistivity is decreased which is due to decrease in porosity with increase in Mn^{2+}concentration. It is also interpreted that in nanocrystalline ferrite system, Mn^{2+} and Fe^{3+} are randomly distributed between A and B sites. Ni^{2+} ions occupy octahedral (B) site. S. Chikazumi observed that Ni exists only in the divalent state. Hence, there is no possibility for the formation of hopping pairs in Ni ferrite. When Mn^{2+} is substituted for Ni^{2+}, some of the Fe^{3+} ions at A-sites migrate to B-sites resulting in the increase of Fe^{3+} concentration at B-sites. Some Mn^{2+} ions also migrate from A-sites to B-sites. This produces increased number of hopping pairs available for conduction process. This results in the reaction [6]

$$Mn^{2+} + Fe^{3+} \Rightarrow Mn^{3+} + Fe^{2+}$$

Consequently, the number of Fe^{2+} and Mn^{3+} ions at B-sites increases. This in turn, increases the hopping of charge carriers between Fe^{2+} and Fe^{3+} ions and between Mn^{2+} and Mn^{3+} ions. This leads to decrease in resistivity. Thus, in spinel ferrites, the main source of electron hopping is the valence exchange between Fe^{2+} and Fe^{3+} ions through the reaction $Fe^{2+} \leftrightarrow Fe^{3+} + e^-$. It is observed the plots change slope at a particular temperature called Curie temperature [7] at which ferromagnetic to paramagnetic transition occurs.

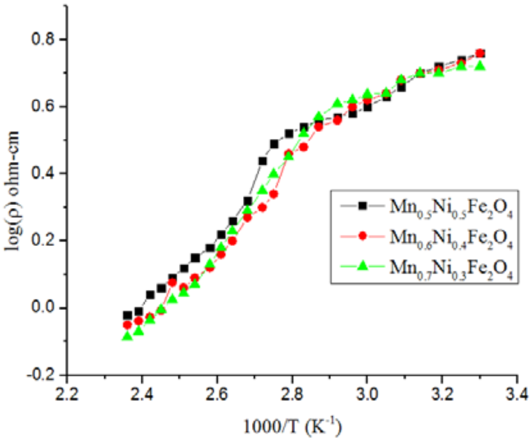

Figure 2: Arrhenius plots of $Mn_xNi_{1-x}Fe_2O_4$ nanoferrite samples sintered at 500°C.

Table 2: Activation energies in ferromagnetic region (E_f), paramagnetic region (E_p) and activation energies (ΔE)

composition	E_f *(eV)*	E_p*(eV)*	*ΔE (eV)*
$Mn_{0.5}Ni_{0.5}Fe_2O_4$4	0.097	0.26	0.16
$Mn_{0.6}Ni_{0.4}Fe_2O_4$4	0.1	0.24	0.14
$Mn_{0.7}Ni_{0.53}Fe_2O_4$	0.09	0.25	0.16

The activation energy is associated with the energy barrier experienced by the electron during hopping process. So, higher activation energy means higher resistivity. The variation of activation energies for the electrical conduction, corresponding to ferrimagnetic region (E_f) and paramagnetic region (E_p) and the Curie temperatures of $Mn_xNi_{1-x}Fe_2O_4$ (x = 0.5, 0.6, 0.7) nanoferrite system with Mn^{2+} concentration are calculated from the slopes of the resistivity plots and are presented in Table 7.2. It is observed from the table that the activation energies in ferrimagnetic region (E_f) are smaller than those in paramagnetic region. This can be attributed to the ordered state of ferrimagnetic region and disordered state of paramagnetic region [8] indicating the effect of the magnetic ordering on the resistivity of the samples. It can be observed from the table that the activation energies are decreasing with increase in Mn^{2+} ion content. These values are small in magnitude indicating small resistivity and hence high conductivity. The obtained activation energy values are consistent with the resistivity values. Thus the process of conduction is influenced by the change in magnetic ordering.

4. Conclusion

At low concentrations of Mn^{2+} concentration, complete ferrite phase is not formed. Concentration of Mn^{2+} influence the ferrite phase. In the present Mn-Ni ferrite systems the D.C.Electrical conductivity varies with cation distribution which in turn changes with the concentration of Mn^{2+}.

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