International Journal of Modern Engineering Research (IJMER)
www.ijmer.com Vol.2, Issue.4, July-Aug. 2012 pp-2303-2306 ISSN: 2249-6645

Synthesis, Characterization ac conductivity of Ni^{2+} doped in magnesium ferrite

Pathan Amjadkhan Noorkhan[1] and Sangshetty Kalayne[2*]
[1]*Department of Physics, Singhania University, Pacheri- Bari, JhunJunnu, Rajasthan*
[2*]*Department of Physics, Rural Engineering College, Bhalki, Bidar, Karnataka, India.*

ABSTRACT: *Magnesium nickel ferrites were synthesized by employing sol gel technique at 1473 K sintering temperature. A critical Rietveld analysis of XRD reveals that the presence of a very small amount of NiO phase along with the ferrite phase. It indicates that almost a stoichiometric (Mg,Ni)-ferrite phase has been obtained at 1473 K. SEM image shows that of (MgNi) ferrite is regular in shape have granular in structure, compact and well connected grain to each others. The ac conductivity increases with increase in applied frequency. The magnesium nickel ferrite ($MnNiFe_2O_4$) shows σ_{ac} conductivity of 1.2 x 10^{-4} S/cm. This is may be attributed to the dipole polarization i.e., the rotation of dipoles between two equivalent equilibrium positions is involved. The high value of dielectric constant of the sample $MnNiFe_2O_4$ may be the structural changes associated with the magnesium nickel ferrite when the grain size is reduced. Therefore, this ferrites material is attracted to use in many science and technological applications.*

Keywords: ***Ac conductivity, (MgNi) ferrite, dielectric constant, Impedance spectra, X-ray diffraction.***

I. INTRODUCTION

Small ferrimagnetic oxides, technically known as ferrites have attracted considerable attention not only from a fundamental scientific interest but also from a practical point of view for growing applications in the magnetic, electronic and microwave fields [1-3]. Simultaneous presence of magnetic and dielectric nature of ferrites is vastly exploited in a variety of applications at different frequencies. The special feature of these materials is that the properties can be tailored over wide ranges by appropriate substitution of various ions in the chemical formula unit and control of processing procedures. Ferrites are extensively used in magnetic recording, information storage, colour imaging, bio-processing, magnetic refrigeration and in magneto optical devices [4, 5].

Ferrites also have great promise for atomic engineering of materials with functional magnetic properties. The formation of corrosion product on the out of core surfaces in pressurized heavy water reactors (PHWRs) are major problem. Ferrite having spinal structure such as magnetic and nickel etc play a major role to prevent such problem. Thus attempts are being made to study the various ferrites to evaluate the impact of substitution of the divalent metal ions to modify the properties of these oxides [6-8].

In the present study authors, report synthesis, characterization and dielectric studies of $MgNiFe_2O_4$. A critical Rietveld analysis of XRD reveals that the presence of a very small amount of NiO phase along with the ferrite phase. It indicates that almost a stoichiometric (Mg,Ni)-ferrite phase has been obtained at 1473 K. SEM image shows that of (MgNi) ferrite is regular in shape have granular in structure, compact and well connected grain to each others. The ac conductivity increases with increase in applied frequency and dielectric constant decreases. Therefore, this ferrites material is attracted to use in many science and technological applications.

II. EXPERIMENTAL

All Chemicals used were analytical grade (AR). The magnesium chloride, nickel chloride (purity 99.99%) and dehydrated ferric chloride were procured and were used as received.

1.1SYNTHESIS OF MAGNESIUM NICKEL FERRITE

The chloride salts of magnesium, nickel chloride and ferric chloride are mixed in calculated stoichiometric with oxalic acid in equimolar ratio so as to form nickel ferric oxalate precursor. The precursor is then filtered and dried at 323K to achieve constant weight. The precursor is mixed with polyethylene glycol (PEG) in the ratio 1:5 and is ignited. The combustion propagates throughout the precursor. After completion of combustion nickel ferrite ($MgNiFe_2O_4$) is formed. The MgNi-ferrite is sonicated in acetone media for 20min and then calcinated at 1473 K to remove the impurities. Finally, fine graded nanosized nickel ferrite particles are formed [9, 10].

The pellets of 10 mm diameter are prepared with thickness varying up to 2 mm by applying pressure of 10 Tons in a UTM – 40 (40 Ton Universal testing machine). For temperature dependent conductivity and sensor studies, the pellets are coated with silver paste on either side of the surfaces to obtain better contacts.

1.2 CHARACTERIZATION

The X-ray diffraction (XRD) pattern of the $MgNiFe_2O_4$ was recorded at room temperature by employing an x-ray powder diffractometer (Rigaku Miniflex) with $CuK_{\square}$ radiation ($\square$=1.5405A^0) in the 2$\square\square$(Bragg angles) range ($2^0 \leq 2\square \leq 10^0$) at a scan speed of 0.5^0 minute^{-1}.

The percentage transmittances for the entire sample are measured from 300 to 4000 cm^{-1}. The SEM images of $MgNiFe_2O_4$ were recorded using Philips XL-30 (ESEM) scanning electron microscopy. The set up used for measuring ac conductivity is Hioki 3050 impedance analyzer, which is in turn interfaced to the computer.

III. RESULTS AND DISCUSSION

2.1 X-RAYS DIFFRACTION

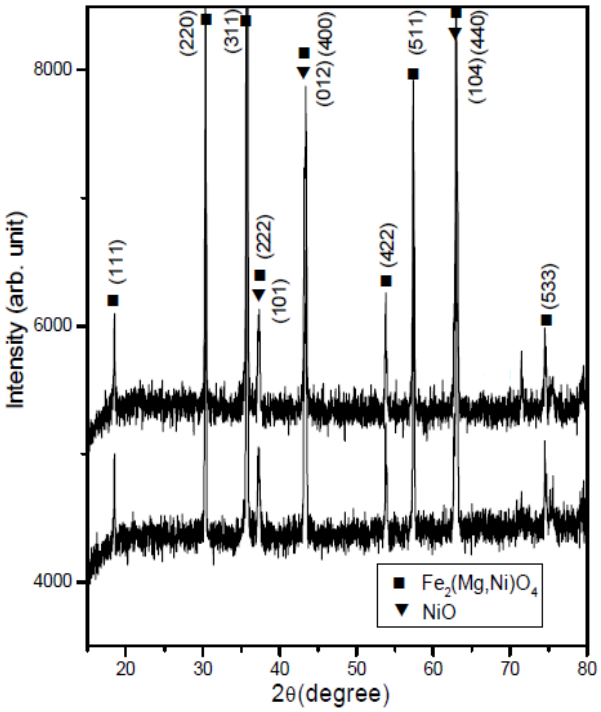

Figure 1 shows the XRD patterns of Mg,Ni)-ferrite annealed at temperature 1473 K.

It seems that the (Mg,Ni)-ferrite phase is formed completely after this heat-treatment. However, a critical rietveld analysis reveals the presence of a very small amount of NiO phase along with the ferrite phase. It indicates that almost a stoichiometric (Mg,Ni)-ferrite phase has been obtained at 1473 K. This indicates that the amount of ferrite phase formation is dependent of annealing time. By measuring particle size we actually measure the coherently diffracting zone of a grain. The particle or crystallites re separated from each other by grain boundaries and the grain boundaries are nothing but bulk crystal imperfections in a crystal [11]. The size of the crystallite in the nanometer range. As can be seen from the experiment, annealing the sample increases the size of the particles. Heat energy helps to annihilate the deformations in the crystals. As a result of grain boundaries started to vanish during annealing and the small crystallites agglomerate together to form larger particles due to intra-grain diffusion.

2.2 SCANNING ELECTRON MICROSCOPY

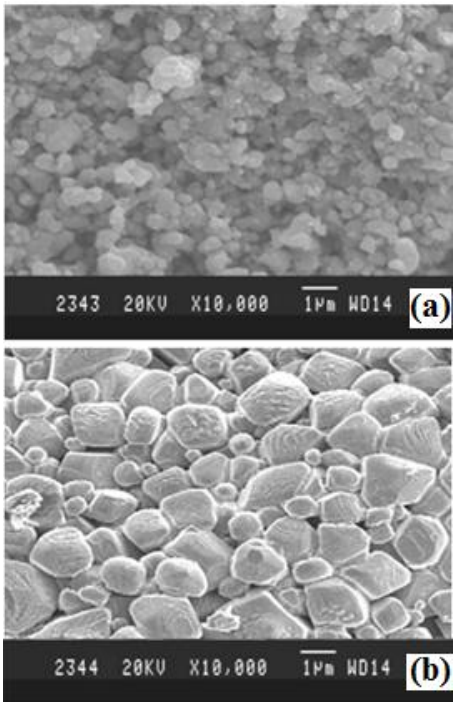

Figure 2 shows the SEM image of (a) NiO and (b) MgNi-ferrite at 1473 K.

Figure 2 (a) shows that SEM image of nickel oxide. It is clearly observed from the image they are agglomerated, highly branched and porous in nature. The average grain size was calculated by using line intercept formula and it is found to be 0.21μm.

Figure 2 (c) shows that SEM image of (MgNi) ferrite. It is found that the image is regular in shape have granular in structure, compact and well connected grain to each others. The average grain size was calculated by using line intercept formula and it is found to be 0.7μm.

2.3 AC CONDUCTIVITY

The variation of σ_{ac} of $MnNiFe_2O_4$ as a function of frequency as shown in figure 3. The conductivity of nickel ferrites is increases with increase in frequency. The magnesium nickel ferrite ($MnNiFe_2O_4$) shows σ_{ac} conductivity of 1.2 x 10^{-4} S/cm.

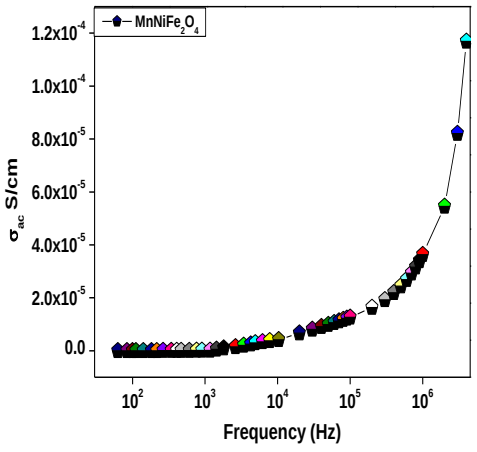

Figure 3 shows the variation of σ_{ac} of $MnNiFe_2O_4$ as a function of frequency.

This is may be attributed to the dipole polarization i.e., the rotation of dipoles between two equivalent equilibrium positions is involved. It is the spontaneous alignment of dipoles in one of the equilibrium positions that give rise to the nonlinear polarization behavior of this composition.

This behaviour of $MnNiFe_2O_4$ obeys the universal power law, □(ω)=□□□□ □ □□(ω)^n (the solid line is the fit to the expression), where r0 is the dc conductivity (frequency independent plateau in the low frequency region), A is the pre-exponential factor, and n is the fractional exponent between 0 and 1 [12]. On crystallization, the conductivity spectrum remains similar as that of the nickel ferrite except dispersion in the low frequency region, where the deviation from □$_{dc}$ (plateau region) is more prominent. The deviation from □$_{dc}$ (plateau region) value in the conductivity spectrum (in the low frequency region) is due to the electrode polarization effect. The values of □□, A, and n were obtained by fitting the □(ω) to □(ω)=□□□□ □ □□(ω)^n. The overall behavior of □$_{ac}$ follows the universal dynamic response, which has widely been observed in disordered materials like ionically conducting glasses and also doped crystalline solids, and is generally believed to be reflected in the mechanism of charge transport behavior of charge carriers.

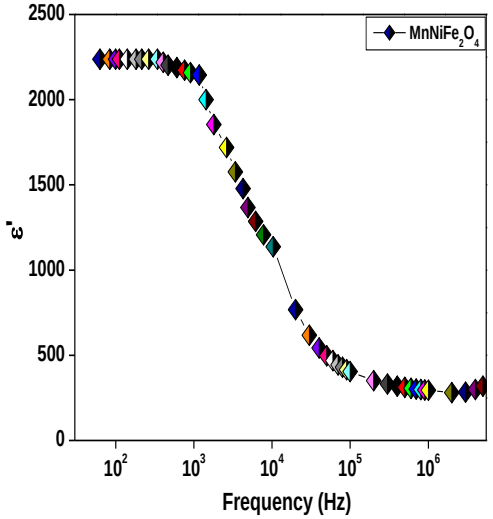

Figure 4 shows the variation real permittivity (□') of nickel ferrite as a function of frequency.

Figure 4 shows the variation real permittivity (□') of nickel ferrite of various composition as a function of logarithmic frequency. It is found that in all these nickel ferrite compositions, as frequency increases, dielectric constant decreases up to the frequency range of 10^5 Hz and after that it remains constant for further increasing in frequency [13]. The strong frequency dispersion of permittivity is observed in the low frequency region followed by a nearly frequency independent behaviour above 10^3 Hz. It is observed that Debye type relaxation mechanism is responsible for higher value of $MnNiFe_2O_4$.

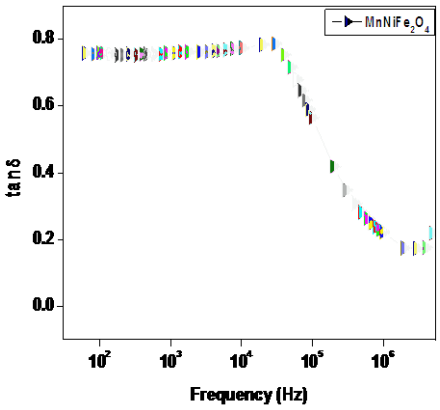

Figure 5 shows the variation of dielectric constant as a function of frequency of $MnNiFe_2O_4$

Figure 5 shows the variation of dielectric constant as a function of frequency for $MnNiFe_2O_4$. The high value of dielectric constant of the sample $MnNiFe_2O_4$ may be explained on the basis of the structural changes associated with the magnesium nickel ferrite when the grain size is reduced. Magnesium nickel ferrite crystallizes into a cubic close-packed arrangement of oxygen ions. It belongs to the class of ferrites with an inverse spinel structure having structural formula, $Fe^{3+}[Mg^{2+}Ni^{3+}]O_4$. The metal ions given in the square bracket are called octahedral (B site) ions and that outside the square bracket are called tetrahedral (A site) ions. The nickel ions (Ni^{2+}) together with half of the iron ions (Fe^{3+}) occupy the B site and the Mg^{2+} occupy the remaining half of the iron ions reside in A site. The presence of Mg^{2+} and Ni^{3+} ions gives rise to p-type carriers (holes) whereas Fe^{2+} and Fe^{3+} ions produce n-type carriers (electrons). Therefore, both electrons and holes that are present in the B sites are due to the presence of Mg and Ni ions. Since Mg ions are present in A sites, electrons are the carriers in A sites. The distance between the ions in A sites (0·357 nm) is larger than the distance between the ions in B site (0·292 nm) [14-16]. Also, the degree of covalency for the A site ions is higher than that of the B site ions. All the above factors result in a high activation energy for the A sites compared to the B sites. Hence, in ordinary magnesium nickel ferrite with an inverse spinel structure the electron movement in B sites dominates compared to that in A sites.

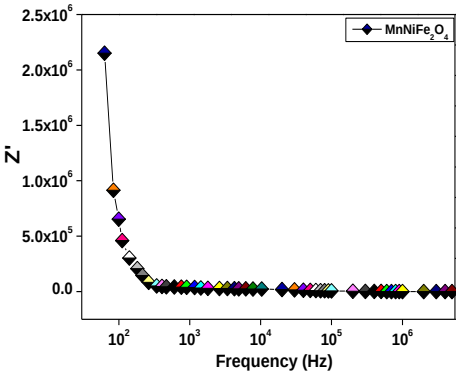

Figure 6 the variation of real part of impedance as a function of frequency

The variation of real part of impedance of $MnNiFe_2O_4$ is shown in figure 6 as a function of increasing frequency. It is observed that the real part of impedance decreases with increase in frequency. The initial decrease in impedance value due to the increase in conductivity at lower frequency region up to 10^3 Hz and further increases in applied frequency, the impedance value remains constant. This indicates that after 10^3 Hz the ferrite acts as lossless materials. Therefore, these ferrites can be used in many technological applications such as memory device, microwave, sensor, transducer, solar cell etc.

IV. CONCLUSION

Sol-gel technique was employed to prepare the magnesium nickel ferrites were at 1473 K sintering temperature. A critical Rietveld analysis of XRD reveals that the presence of a very small amount of NiO phase along with the ferrite phase. It indicates that almost a stoichiometric (Mg,Ni)-ferrite phase has been obtained at 1473 K. SEM image shows that of (MgNi) ferrite is regular in shape have granular in structure, compact and well connected grain to each others. The ac conductivity increases with increase in applied frequency. The magnesium nickel ferrite ($MnNiFe_2O_4$) shows σ_{ac} conductivity of 1.2 x 10^{-4} S/cm. This is may be attributed to the dipole polarization i.e., the rotation of dipoles between two equivalent equilibrium positions is involved. The high value of dielectric constant of the sample $MnNiFe_2O_4$ may be the structural changes associated with the magnesium nickel ferrite when the grain size is reduced. It is observed that the real part of impedance decreases with increase in frequency. The initial decrease in impedance value due to the increase in conductivity at lower frequency region up to 10^3 Hz and further increases in applied frequency, the impedance value remains constant. Therefore, this ferrites material is attracted to use in many science and technological applications.

REFERENCE

[1] I. Anton, I. D. Dabata and L. Vekas, "Application Orientated Researches on Magnetic Fluids," *Journal of Magnetism and Magnetic Materials*, 85 *(1)*, 1990, 219-226.

[2] R. D. McMickael, R. D. Shull, L. J. Swartzendruber, L. H. Bennett and R. E. Watson, "Magnetocaloric Effect in Superparamagnets," *Journal of Magnetism and Magnetic Materials*, 111*(1)*, 1992, 29-33.

[3] D. L. Leslie-Pelecky and R. D. Rieke," Magnetic Properties of Nanostructures Materials," *Chemistry of Materials*, 8 *(8)*, 1996, 1770-1783.

[4] T. Hirai, J. Kobayashi and I. Koasawa, "Preparation of Acicular Ferrite Fine Particles Using an Emulsion Liquid Membrane System," *Langmuir*, 15 *(19)*, 1999, 6291-6298.

[5] R. H. Kodama, "Magnetic Nanoparticles," *Journal of Magnetism and Magnetic Materials*, 200 *(1)*, 1999, 359-372.

[6] K. V. P. M. Shafi, Y. Koltypin, A. Gedanken, R. Prozorov, J. Balogh, J. Lendvai and I. Felner, "Sonochemical Preparation of Nanosized Amorphous $NiFe_2O_4$ Particles," *The Journal of Physical Chemistry B*, 101 *(33)*, 1996, 6409-6414.

[7] D. Niznansky, M. Drillon and J. L. Renspinger, "Preparation of Magnetic Nanoparticles (γ-Fe_2O_3) in the Silica Matrix," *IEEE Transaction on Magnetics*, 30 *(2)*, 1994, 821-823.

[8] J. M. Yang, W. J. Tsuo and F. S. J. Yen, "Preparation of Ultrafine Nickel Ferrite Powder Using Ni and Fe Tartrates," *Journal of Solid State Chemistry*, 145*(1)*, 1999, 50-57.

[9] Y. Shi, J. Ding, X. Liu and J. Wang, "NiFe2O4 Ultrafine Particles Prepared by Co- Precipitation / Mechanical Alloying," *Journal of Magnetism and Magnetic Materials*, 205 *(2)*, 1999, 249-254.

[10] P. Druska, U. Steinike and V. Sepelak, "Surface Structure of Mechanically Activated and of Mechano-synthesized Zinc Ferrite," *Journal of Solid State Chemistry*, 146 *(1)*, 1999, 13-21.

[11] V. Sepelak, K. Tkacova, V. V. Boldyrev and U. Steinike, "Crystal Srtucture Refinement of the Mechanically Activated Spinel-Ferrite," *Materials Science Forum*, 228, 1996, 783-788.

[12] V. Sepelak, A. Yu, U. Rogachev, D. Steinike, C. Uecker, S. Wibmann and K. D. Becker, "Structure of Nanocrystalline Spinel Ferrite Produced by High Energy Ballmilling Method," *Acta Crystallographica A*, 52, 1996, C367

[13] V. Sepelak, U. Steinike, D. C. Uecker, S. Wibmann and K. D. Becker, "Structural Disorder in Mechanosynthesized by Zinc Ferrite," *Journal of Solid State Chemistry*, 135 *(1)*, 1998, 52-58.

[14] H. M. Rietveld, "Line Profile of Neutron Powder Diffraction Peaks for Structure Refinement," *Acta Crystallographica*, 22, 1967, 151-152.

[15] H. M. Rietveld, "A Profile Refinement Method for Nuclear and Magnetic Structures," *Journal of Applied Crystallography*, 2, 1969, 65-71.

[16] L. Lutterotti, P. Scardi and P. Maistrelli, "LSI-a Computer Program for Simultaneous Refinement of Material Structure and Microstructure," *Journal of Applied Crystallography*, 25 (3), 1992, 459-462.