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Study on the Transport Properties of $NiFe_2O_4$ Synthesized by Sonochemical Method

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Abstract

Nickel Ferrite ($NiFe_2O_4$) has been synthesized by sonochemical method. Samples were calcined in the temperature range of 200-1400°C for 3 hours. X-ray diffraction pattern yielded broad diffused pattern for the sample calcined at 200°C for 3 hours. With the increase of calcinations temperature, peak width decreases as a result of grain growth. In order to study the transport properties like resistivity and dielectric constant of $NiFe_2O_4$ synthesized by sonochemical method, samples have been sintered in the temperature range of 800-1300°C for 3 hours. SEM microstructure reveals homogeneous distribution of equiaxial grains. The DC electrical resistivity of $NiFe_2O_4$ samples decreases with increase in sintering temperature. Decrease in resistivity with increase in sintering temperature is attributed to the micro structural factors such as grain size, porosity, grain boundary area as well as conversion of trivalent Fe^{3+} ions to the divalent Fe^{2+} state. The analysis of the dielectric property in the frequency range of 100 kHz-7 MHz has shown that the real part of the dielectric constant decreases with increase in frequency of applied field. The variation has the characteristics of relaxation and is attributed to the granular structure of ferrites. The dependence of dielectric properties on sintering temperature for the frequency range of 100 kHz to 5 MHz follows the conventional nature of ferrites.

Key words- $NiFe_2O_4$; Sonochemical; Nanoparticle.

1. Introduction

Numbers of applications, especially at high frequencies, are looking for ferrites with enhanced transport properties. Ferrites are attractive in these application areas for their high electrical resistivity. The transport properties of ferrites can be enhanced using modified techniques. Sonochemical synthesis is such a method to synthesize ferrites with enhanced transport properties such as resistivity and dielectric property.

For the perfect preparation of ferrites with optimized properties, dexterous handling and wary approach is the rudimentary need. As the ferrites are not completely defined by its chemistry and crystal structure, the knowledge and control of parameters of its microstructure such as density, grain size, porosity and their intra and inter-granular distribution are the momentous requirements. Various methods have been developed to synthesize nanocrystalline $NiFe_2O_4$, including a sonochemical method, citrate precursor techniques, co-precipitation, mechanical alloying, sol-gel, pulsed wire discharge, shock wave, reverse micelle, hydrothermal, microwave induced combustion process [1-3]. However, it is still crux to find suitable and cost effective routes by the utilization of cheap, innocuous and environmentally nonthreatening precursors to synthesize $NiFe_2O_4$. A standard sonochemical method is used to produce fine particles of $NiFe_2O_4$ in the present work. Sonochemistry is the research area in which molecules undergo chemical reaction due to the application of powerful ultrasound radiation (20 kHz-10 MHz). The physical phenomenon responsible for the sonochemical process is acoustic cavitations. Recently, the use of ultrasound has been proved to be beneficial to obtain ultrafine particles of ferrites [4-5], which provide better opportunity to control particle size. Nascentes et. al. [6] have established the optimized conditions for the use of the ultrasonic bath for analytical applications. They have demonstrated that under the optimized conditions maximum cavitation intensities in ultrasonic baths can be obtained. A number of theories have been developed in order to explain how 20 kHz sonic radiation can break chemical bonds. They all agree that the main event in sonochemistry is the creation, growth, and collapse of a bubble that is formed in the liquid [7].

The purpose of the present work is to synthesize single phase spinel $NiFe_2O_4$ by the sonochemical method and then sintered at different temperatures to analyze the variation of the transport properties of the samples.

2. Experimental

A standard sonochemical method is used to produce fine particles of $NiFe_2O_4$. Analytical grade of $Fe(NO_3)_3.9H_2O$ and $Ni(NO_3)_2.6H_2O$ were mixed in required molar ratio and added to 6M NaOH solution in an ultrasonic bath at room temperature. The reaction time was allowed as 5 hours followed by centrifugation at 15000 rpm for 15 minutes. The precipitate was washed 10 times with distilled water. Finally, the precipitate was collected and heated at 90°C for 36 hours. X-ray diffraction patterns of as-dried powder yielded broad diffused pattern near the maximum intensity peak of $NiFe_2O_4$.

Pellets, Tablets and Ring shaped samples were prepared by using different dies for different measurements and sintered at various temperatures in the range of 800-1300°C. Microstructure has been studied by Scanning Electron Microscope.

Resistivity has been measured using pellet shaped samples with a thickness of about 2 mm and diameter of about 10 mm. The dielectric constant is measured indirectly from the capacitance of a capacitor in which the material is used as electrode separator or dielectric.

3. Results and Discussions

X-ray diffraction patterns of the sample prepared by sonochemical method and calcined in the temperature range of 200-1200°C has been presented in Fig. 1. It has been found that after the calcination of the sample at 200°C for 3 hours X-ray diffraction pattern is characterized by broad peak which is characteristic to very fine grain size of the order of 2-3 nm. With the increase of sintering temperature the peaks become narrower which reveals increase of particle size.

The size of the nanoparticles have been determined by using Scherrer's formula [8] from the FWHM of (311) peaks and presented in Fig. 3. The particles prepared from sonochemical method in the as-dried condition is much finer i.e. amorphous/semi crystalline state than prepared by chemical co-precipitation the grain size of which has been obtained as ~7 nm [9].

The diffraction peaks corresponding to planes (220), (311), (222), (400), (422), (511), and (440) at higher sintering temperature provide a clear evidence for the formation of spinel structure of the ferrite which is free from the presence of any extra peak. It has been shown from the Fig. 3 that the grain size has been obtained from ~2 nm to 51 nm for the $NiFe_2O_4$ nanoparticle sample with the systematic variation of sintering temperature. The grain size increases very rapidly from 600°C-1200°C with increase in the sintering temperature.

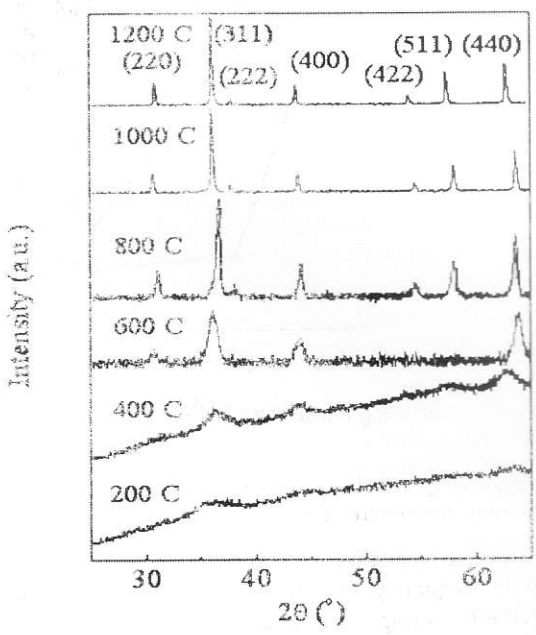


Fig. 1: X-ray diffraction patterns of the samples calcined at different temperatures.

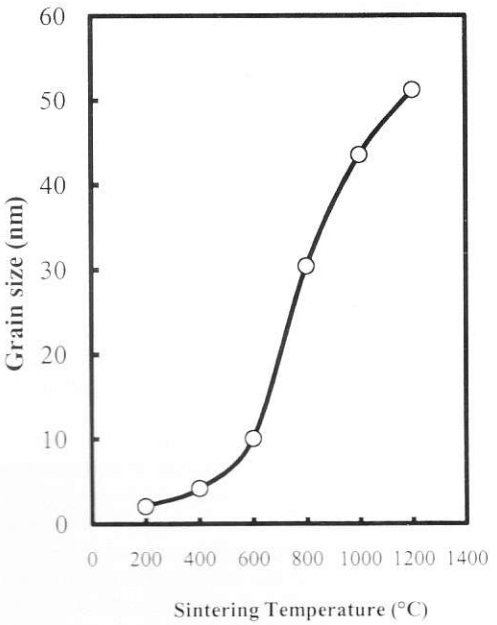
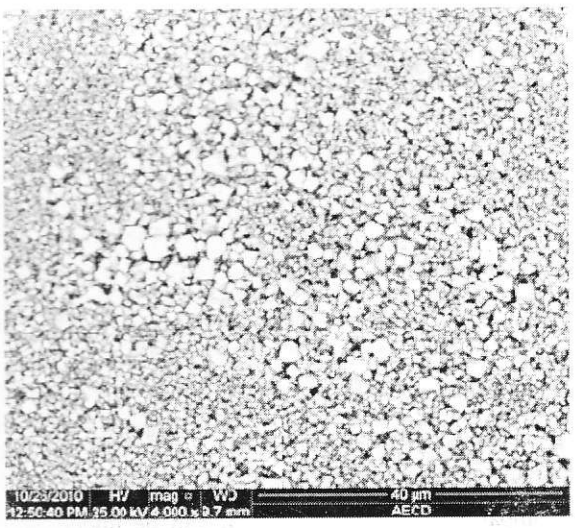
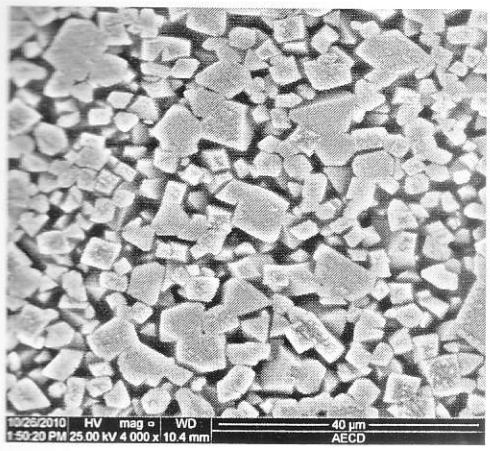


Fig. 2: Variation of Grain Size with sintering temperature, Ts.

Microstructures of $NiFe_2O_4$ sintered at 1000° C and 1300° C have been studied by Scanning Electron Microscope and presented in Fig. 3 with the magnification ×4000. It can be observed that the microstructures of the samples sintered at both the temperatures are almost homogeneous. This result can be compared with ref [9] where microstructures have been presented for different sintering temperatures. Though grain size and distribution are almost homogenous for the samples prepared by chemical co-precipitation presented in ref [9], average grain size for the sample sintered at 1300°C is almost two times than the grain size of 1300°C sintered sample under identical condition. This implies that the sonochemical method has provided a significant improvement of microstructure in terms of size and distribution.



(a)



(b)

Fig. 3: Microstructure determination at sintering temperatures (a) 1000^0 C and (b) 1300^0 C

In Fig. 4 variation of DC electrical resistivity as a function of inverse temperature has been presented. From Fig. 5 it can also be observed that room temperature resistivity decreases with the increase in sintering temperature for all the samples sintered in the range of 800-1300°C.

Decrease in resistivity with the increase of sintering temperature may be attributed to the micro-structural factors such as grain size, porosity, grain boundary area as well as conversion of trivalent Fe^{3+} ions to the divalent Fe^{2+} state. Increase in sintering temperature results in greater density and grain growth which decrease the porosity and the number of grain boundaries. And since the pores are non-conductive, the charge carriers will face fewer pores on their way for higher sintering temperature and thereby leading to decrease in resistivity.

In addition to this, with the increase of sintering temperature partial reduction of trivalent Fe^{3+} ions to the divalent Fe^{2+} takes place. Formation of Fe^{2+} ions gives rise to the conduction of ferrite due to electron hopping between Fe^{3+} and Fe^{2+} ions co-existing at the closer spaced B sites in the spinel lattice and thereby decrease the resistivity.

The activation energy decreases with the increase of sintering temperature quoted in Fig. 4 and Fig. 5. Decrease of activation energy with the increase of sintering temperature may be attributed to the higher conduction of charge carriers due to partial elimination of defects and co-existence of different valence state of cations.

The result in the present research shows that the value of resistivity ranges from 10^6 ohm-cm to 10^{11} ohm-cm for the samples synthesized by sonochemical method. But the resistivity of the samples prepared by chemical co-precipitation technique was below 10^5 ohm-cm except for the samples that were sintered at 1350^0 C for which the resistivity was about 10^7 ohm-cm.

By comparing these two results it can be understood that resistivity increases much for the samples chemically synthesized by ultrasonic vibration than that of the samples prepared by chemical co-precipitation technique that reported in ref [9].

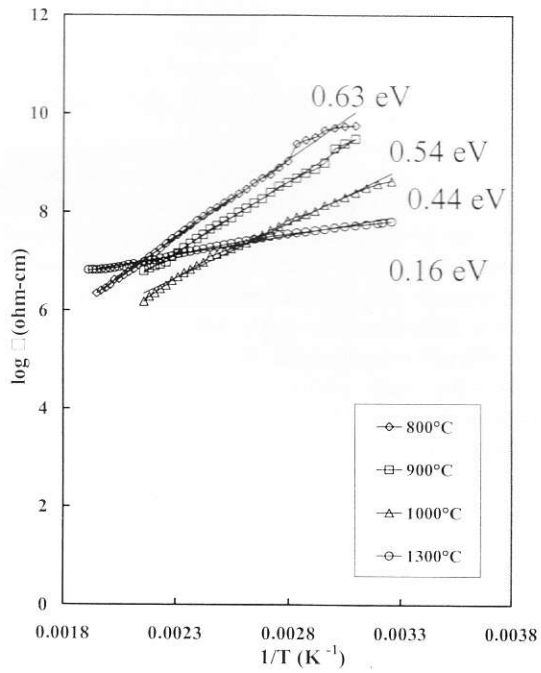


Fig. 4: Variation of DC electrical resistivity with Temperature.

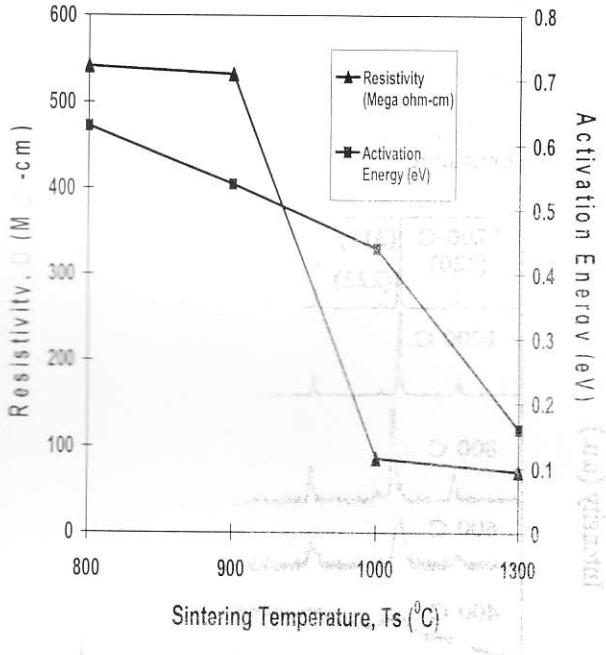


Fig. 5: Variation of DC electrical resistivity and Activation Energy with sintering temperature (at room temperature, T = 25^0 C).

Fig. 6 shows the variation of real part (ϵ') of dielectric constant with frequency for various sintering temperatures for the $NiFe_2O_4$ sample. The dielectric constant is an intrinsic property of a material and a measure of the ability of the material to store electric charge relative to vacuum

i.e. the stored energy is described by the real part of the dielectric constant.

The results found in this experiment can be compared with the results of ref [10]. The dielectric constants of the samples of $NiFe_2O_4$ in this experiment are much smaller than those of Nickel Ferrite prepared from chemicals of analytical grade [10].

From the Fig. 4 and Fig. 6 it can be seen that the higher value of dielectric constants are associated with lower resistivity. The dielectric constants have been dispersed for all the samples. In order to explain dielectric dispersion in ferrites, the grain and grain boundaries are assumed to be two different layers each having a different conductivity but similar dielectric constant. As the frequency rises from a low value, the bulk resistivity and dielectric constant commence to decay and become asymptotic to lower values at high frequencies. This variation has the characteristic of relaxation and is attributed to the granular structure of ferrites in which crystallites are separated by boundaries having much higher resistivity than the crystallites. Thus the structure behaves as a compound dielectric. At low frequencies the impedance of the crystallites is negligible compared to that of the boundary [10]. The dielectric constant approaches to the value which is analogous to calculating dielectric properties from measurements on a specimen between the plates of capacitor, using a dielectric length 1/n times the actual value. The boundary capacitance becomes short circuited with the boundary resistance and the bulk dielectric properties approach those of crystallites at very high frequencies.

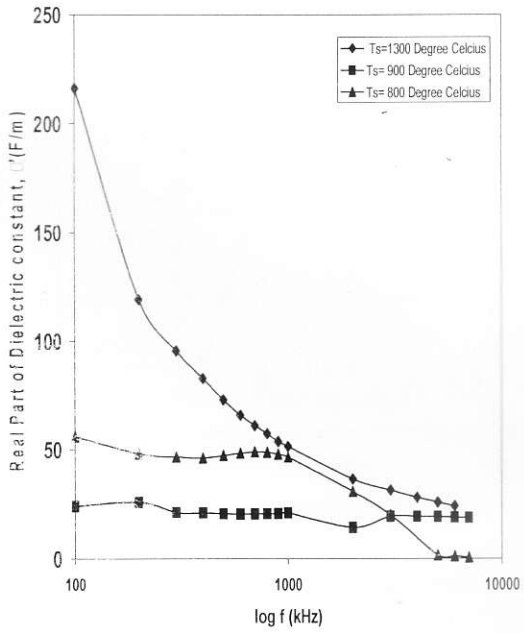


Fig. 6: The dependence of real part of dielectric constant (ϵ') on frequency.

The dependence of dielectric properties on sintering temperature has been presented for the frequency range of 100 kHz to 5 MHz in Fig. 7. In ferrites where electrical resistivity is considerable, space charge polarization arising from differences between the resistivity of various phases. The frequencies at which the polarization occurs, is proportional to the product of conductivities of different phases. For ferrite dielectrics this polarization increases for the samples sintered at higher temperatures. Since the resistivity decreases at higher sintering temperatures (shown in Fig. 5), the dielectric constant increases. In this experiment, it can be observed that the alteration of dielectric constant with sintering temperature follows the conventional nature of ferrites. The result for nickel ferrite, chemically synthesized by ultrasonic vibration, shown in Fig. 8 follows the general behavior of spinel ferrites. From Figure it can easily be found that the permittivity has its lowest value at the highest frequency that is at 5 MHz.

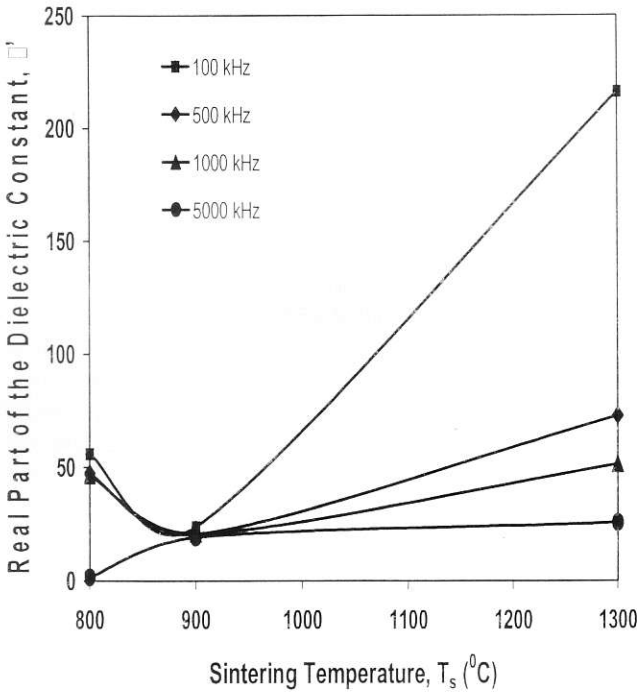


Fig. 7: Variation of real part of dielectric constant (ϵ') with sintering temperature at frequencies ranging from 100 KHz to 5 MHz.

4. Conclusion

Sonochemical technique has been used to synthesize Nickel Ferrite. The sonochemical method has provided a significant improvement of particle size in terms of size and distribution which has been confirmed by the Scanning Electron Microscopy results. Transport properties observation has shown that all the samples showed dielectric dispersion in studied frequency range. Moreover, the DC electrical resistivity shows that the value of resistivity has increased by an order of magnitude than the sample prepared by conventional ceramic technique.

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References

1. Klabunde, K. J., 2001. Nanoscale Materials in Chemistry, Ch. 4, 95, John Wily and Sons.
2. Delau, J. G. M., 1970. Preparation of Ceramic Powders from Sulfate Solutions by Spray Drying and Roasting. *Amer. Ceram. Soc. Bull.* ***49 (6),*** *572-574.*
3. Roy, R., 1974. New Ceramic Materials Produced by Novel Processing Techniques, *Int. J. of Powder Metallurgy.* ***6 (1),*** *25-28.*
4. W. Lv, B. Liu, Z. Luo, X. Ren and P. Zhang, 2008, *J. Alloys Compd.*, ***465***, *261-264.*
5. S. Theerdhala, D. Alhat, S. Vitta, and D. Bahadur, 2007. *J. Nanosci. Nanotech,* ***8***, *1-5.*
6. C. C. Nascentes, M. Korn, S. S. Clarivaldo and M. A. Z. Arruda, 2001. *J. Braz. Chem. Soc.*, ***12(1),*** *57-63.*
7. Rao, C. N. R., Miller, A., Chitham, A. K., 2004. The Chemistry of Nanomaterials: Synthesis properties and Application, Vol. 1, Willey-VCH, *113-116.*
8. Patterson, A.L., 1939. The Scherrer Formula for X-Ray Particle Size Determination, *PRL*, ***56***, *978-982.*
9. Hoque, S. Manjura, Hakim, M. A., Saha, I. and Nordblad, P., 2010. Effect of grain size on Neél temperature, magnetic and electrical properties of NiFe2O4 nanoparticle synthesized by chemical co-precipitation technique. *NSTI-Nanotech 2010, 1, 518-521.*
10. Hoque, S. Manjura, Choudhury, M. A., Hakim, M. A and Islam, M. F., 2004, *Proceedings of 2nd International Conference on Structure, Processing and Properties of Materials, 705-712.*