JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 10, October 2008, p. 2644 - 2648

Structural and dielectric properties of Ni-Zn ferrite nanoparticles prepared by co-precipitation method

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The dielectric properties of $Ni_{1-x}Zn_xFe_2O_4$ ferrites (with x=0.0 to 0.7, dx=0.1) prepared by wet chemical co-precipitation method have been studied as a function of frequency, temperature and composition. The broad XRD peaks of green samples and TEM images confirm the nano dimension of prepared samples. Dispersion in the dielectric constant with frequency is observed and dielectric loss also shows decrease in its value with increasing frequency. The dielectric loss tangent was found to increase with frequency. Dielectric constant (ε′), dielectric loss (ε″) and loss tangent (tanδ) show strong temperature dependence at all frequencies. The temperature dependent results indicate that the values of ε′, ε″ and tanδ increases with increasing temperature.

(Received April 24, 2008; accepted August 14, 2008)

Keywords: Dielectric constant, Dielectric loss, Loss tangent, Co-precipitation, Ni-Zn ferrite

1. Introduction

Ferrites have good dielectric properties and a large number of applications from microwave to radio frequencies. Of all ferrites, Ni-Zn is the most versatile because of their many technological applications. These ferrites are known to have high resistivity and, therefore, low eddy current losses, and relatively low initial permeability. Ni-Zn ferrite have unique high dielectric properties which makes them useful in designing electronic devices [1-2]. Due to low power loss (LPL) property, Ni-Zn ferrites can be used in switch mode power supplies (SMPS) for the working frequencies climbing above 1MHz. Hot pressed and single crystal Ni-Zn ferrites are found quite suitable for magnetic recording head due to high thermal stability, wear and corrosion resistance with low magnetostriction and high frequency response. For high frequency applications knowledge of dielectric properties of ferrites is necessary and the parameters that need to be evaluated are dielectric constant (ε′), dielectric loss (ε″) and loss tangent (tanδ). High frequency applications of Ni-Zn ferrites include large number of microwave components such as circulators, isolators, gyrators, phase shifters, YIG tuned filters, and switches and substrates for microwave integrated circuits [3]. It is found that not much work have been reported on the dielectric properties of Ni-Zn except few [4-6].

Soft ferrites are usually prepared by ceramic method, which suffers from many drawbacks [7-8]. Recently some chemical methods have been used to synthesize soft ferrites for the reason that they produce nano-size particles [9-11]. The systems made up of nano-particles are intensively studied both theoretically and practically, due to their electrical and magnetic properties that are sensibly different from those of their bulk counterpart [12-13]. The dielectric properties of the soft ferrites depend upon preparation method and sintering conditions. The wet chemical co-precipitation method is a suitable method to produce reproducible stoichiometric compositions of ferrites having nano size particles. In the present work a systematic study of the dielectric properties of $Ni_{1-x}Zn_xFe_2O_4$ ferrite system is made by means of dielectric constant (ε′), dielectric loss (ε″) and loss tangent (tanδ) as a function of temperature, frequency and composition.

2. Experimental

The spinel ferrite system $Ni_{1-x}Zn_xFe_2O_4$ with variable composition (x = 0.0-0.7) is prepared by air oxidation of an aqueous suspension containing Ni^{2+}, $Zn^{2+}$and Fe^{3+} cations in proper proportions. The starting solutions were prepared by mixing 50ml of aqueous solution of $FeSO_4{\cdot}7H_2O$, $NiSO_4{\cdot}7H_2O$ and $ZnSO_4{\cdot}7H_2O$ in stoichiometric proportion. In preparing the solution, the molarity of Fe^{3+} is assumed as 0.5M and that of Ni^{2+} and Zn^{2+} is assumed as 0.25M. A two molar (2M) solution of NaOH was used as a precipitant. It has been suggested that the solubility product constant K_{sp} of all the constituents always exceed when the starting solution is added into the precipitant. Therefore, in order to achieve simultaneous precipitation of all the hydroxide $Ni(OH)_2$, $Zn(OH)_2$, and $Fe(OH)_2$, the starting solution (pH≈3) was added to the solution of NaOH and a suspension (pH=11) containing dark intermediate precipitation was found. Then the suspension was heated and kept at a temperature of 60^0C, while oxygen gas was bubbled uniformly, the suspension was stirred to promote the oxidation reaction until all the intermediate precipitant changed into the dark brownish precipitate of the soft ferrite. The samples were filtered, washed several times by distilled water. The wet samples of Ni-Zn system were annealed at 800^0C for 12 hrs.

Table 1. Lattice constant (a), X-ray density (d_x), Measured density (d_m), Porosity (P), particle size (t) and Specific surface area (S) of $Ni_{1-x}Zn_xFe_2O_4$

Comp. 'x'	a (Å)	'd_x' (gm/cm^3)	'd_m' (gm/cm^3)	P (%)	t (nm)	S (m^2/gm)
0	8.347	5.307	4.121	22.29	22	50
0.1	8.365	5.312	4.171	21.49	26	37
0.2	8.379	5.319	4.213	20.81	24	33
0.3	8.391	5.324	4.245	20.19	25	27
0.4	8.402	5.335	4.294	19.56	23	26
0.5	8.411	5.339	4.321	19.26	26	23
0.6	8.411	5.348	4.341	18.31	27	24
0.7	8.407	5.356	4.374	17.52	25	25

The X-ray powder diffraction patterns of the as prepared samples and annealed samples were recorded on Philips X-ray diffractometer (Model Joel-DX-8030) at room temperature. The dielectric constant (ε′) dielectric loss (ε″) and dielectric loss tangent (tanδ) were measured as a function of frequency and temperature by using LCR-Q meter (Model HP 4284). The dielectric measurements as a function of frequency were made using two-probe method at the frequencies 100Hz, 120Hz, 1KHz and 10KHz at room temperature.

3. Results and discussion

Fig. 1 depicts the X-ray diffraction patterns of typical as prepared wet samples x = 0.1, x = 0.3 and x = 0.5. The broad peaks of XRD patterns clearly indicate that the particle size is of nano meter dimension. The virgin samples are sintered at 800^0C and again characterized by X-ray diffraction technique. The sintered samples show sharp XRD peaks indicating completion of crystallization. The analysis of X-ray diffraction data identified that all the samples have single-phase cubic spinel structure. The values of lattice constant obtained from XRD data are given in Table1. It is observed from these values that lattice constant of the samples increased with increase of the Zn content x. The increasing behaviour of lattice constant can be explained on the basis of the fact that ionic radius of Zn^{2+} ion (0.74Å) is greater than that of Ni^{2+} ion (0.69Å) and hence expansion in the unit cell dimension takes place. The particle size values estimated from XRD data lies between 22-27 nm. Particle morphology and particle size are also estimated by transmission electron microscopy. The TEM images of typical sample (Fig. 2) x = 0.3 shows that the Ni-Zn ferrite nano particles are of uniform size of nano dimensions and highly crystalline.

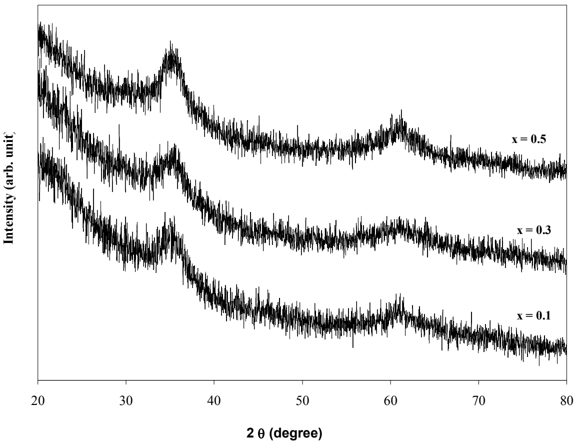

Fig. 1. XRD patterns for the samples x = 0.1, 0.3 and 0.5 of the series $Ni_{1-x}Zn_xFe_2O_4$

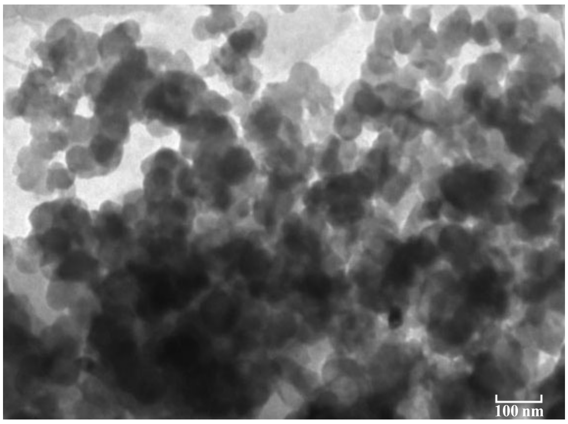

Fig. 2. TEM image of typical sample x = 0.3 of the series $Ni_{1-x}Zn_xFe_2O_4$

The values of structural parameters like x-ray density (d_x), measured density (d_m), porosity (P), particle size (t) and specific surface area (S) as a function of zinc concentration 'x' are given in Table 1. It is observed from

Table 1 that X-ray density increases with increasing Zn content 'x'. It is observed that porosity decreases as the concentration of zinc is increases. It is due to larger ionic radius of Zn as compared to Ni. The specific surface area are calculated and found that the specific surface areas values ranges in between 50 m^2/gm to 20 m^2/gm.

Thermal variation of the dielectric constant of all the samples has been studied at four different frequencies 100Hz, 120Hz, 1 KHz, and 10 KHz. It is observed that for each sample the dielectric constant decreases rapidly with increasing frequency up to 1KHz, and is nearly constant for 10KHz. Typical frequency variation curves, corresponding to sample x = 0.4, at different temperatures are shown in Fig. 3. It can be seen from the figure that dielectric constant (ε') decreases with increasing frequency. The observed dispersion of the dielectric constant can be explained on the basis of hopping conduction between Fe^{3+} and Fe^{2+}, Ni^{2+} and Ni^{3+} pairs of ions. It is well known that in ferrites with heterogeneous structure the samples consist of well-conducting grains separated by poorly conducting grain boundaries [14]. The electrons reach the grain boundary through hopping and if the resistance of the grain boundary is high enough, electrons pile up at the grain boundaries and produce polarization. However, as the frequency of the applied field is increased, the electrons reverse their direction of motion more often. This decreases the probability of electrons reaching the grain boundary and as a result polarization decreases. Therefore, the dielectric constant decreases with increasing frequency of the applied field. The fine particle nature of ferrite particles prepared by co-precipitation method results in large number of grain boundaries. These grain boundaries act as scattering centers.

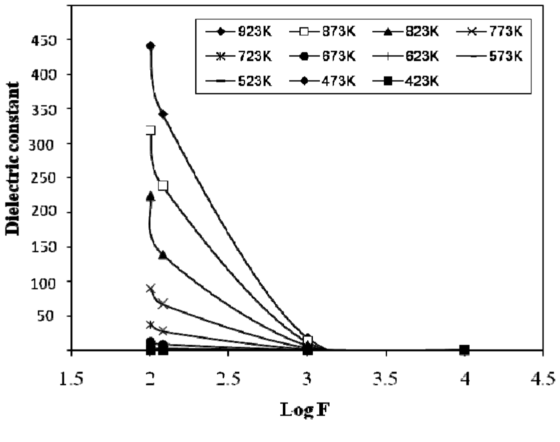

Fig. 3. Variation of the dielectric constant with frequency of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ at different temperatures.

The variation of dielectric constant with temperature for frequencies 100Hz, 120Hz, 1 KHz and 10 KHz was studied. It is clear that dielectric constant increases with temperature at all frequencies. The increase in the value of dielectric constant with an increase in temperature is very large at lower frequency (100Hz), while for higher value of frequency (1 KHz) the increase is very small. Typical dielectric constant versus temperature curves at different frequencies for sample corresponding to x =0.3, are shown in Fig. 4. The dielectric constant of any material, in general, is due to dipolar, electronic, ionic and interfacial polarizations. At low frequencies dipolar and interfacial polarizations are known to play the most important role [15]. Both these polarizations are strongly temperature dependent. Whereas the interfacial polarization increases with temperature due to creation of crystal defects, dipolar polarization decreases with increase in temperature. The rapid increase in the dielectric constant with increase in temperature at low frequencies suggests that the effect of temperature is more pronounced on the interfacial than on the dipolar polarization. At high frequencies electronic and ionic polarizations are the main contributors [15] and their temperature dependence is insignificant. Therefore, a constant and low value of the dielectric constant at high frequencies is observed.

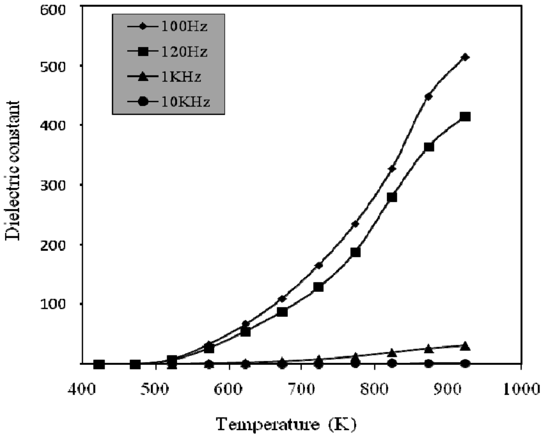

Fig. 4. Variation of the dielectric constant with temperature of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ at different frequencies.

The variation of dielectric constant with temperature for different compositions is shown in Fig. 5. It is found that dielectric constant increases with increasing Zn composition x up to x=0.3 at which it has maximum value. A distinct maxima is observed for every temperature for Zn composition x=0.3. Further increase in x shows decrease in value of dielectric constant. In Ni-Zn ferrites Zn occupies (A) site and Ni occupies [B] site, while Fe occupies both (A) and [B] sites. When Zn^{2+} is added in place of Ni^{2+}, with increasing Zn composition x, some of the Fe^{3+} ions get converted in to Fe^{2+} ions so as to maintain the charge neutrality. It thus follows that addition of Zn at the cost of Ni converts Fe^{3+} to Fe^{2+} ions. This increases the hopping between Fe^{3+} and Fe^{2+} ions, thereby decreasing the resistance of the grain. This increases the probability of electrons reaching the grain boundary. As a result, the polarization and, hence, the dielectric constant increases. This has been observed for compositions up to 0.3. Decrease in dielectric constant (ε') for further increase in composition may be due to the decrease in hopping between Fe^{3+} and Fe^{2+} ions [16].

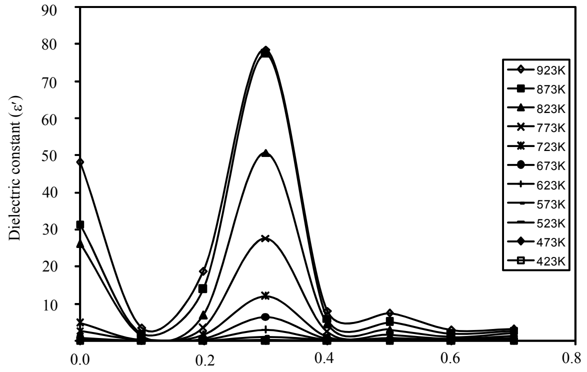

Fig. 5. Variation of the dielectric constant with composition at 1KHz for different temperatures.

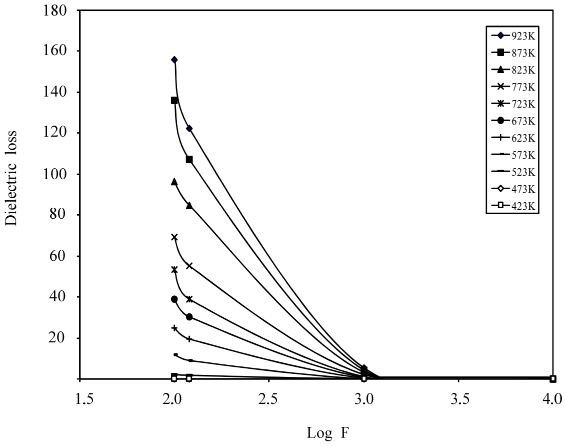

Fig. 6. Variation of the dielectric loss with frequency of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ at different temperatures.

The variation of dielectric loss (ε″) with frequency is shown in Fig. 6 for x=0.7. It can be seen from this figure that dielectric loss decreases with increasing frequency. A more dielectric dispersion is observed at low frequency region. The variation of dielectric loss with temperature for composition x=0.3 is shown in Fig. 7. It is observed that dielectric loss increase with increasing temperature at 1KHz. The same type of behaviour is observed for all Zn compositions. The decrease in dielectric loss takes place when the jumping frequency of electric charge carriers can not follow the alteration of applied electric field beyond certain critical frequency [17-18]. The observed variation of the loss tangent tanδ with frequency at different temperatures for all compositions x of system $Ni_{1-x}Zn_xFe_2O_4$ was studied. It is observed that all samples show identical behaviour. The loss tangent increases with increasing frequency. A typical variation curve corresponding to sample x=0.3 is shown in Fig. 8. According to the Iwauchi [19], there is a strong co-relation between the conduction mechanism and the dielectric behaviour of ferrites. A maximum value in dielectric loss tangent (tanδ) can be observed when the hopping frequencies are approximately equal to that of the externally applied electric field [20].

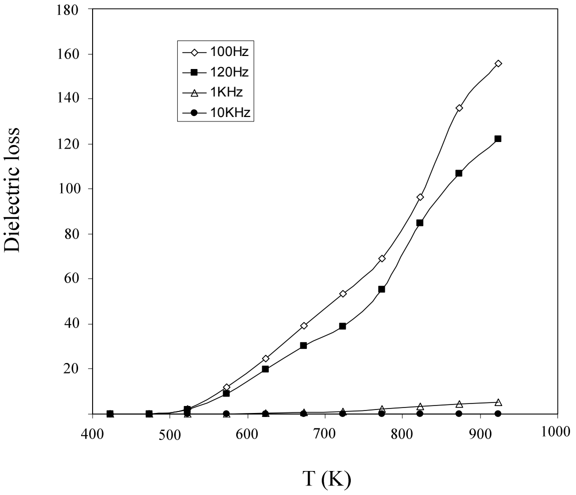

Fig. 7. Variation of the dielectric loss with temperature of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ at different frequencies.

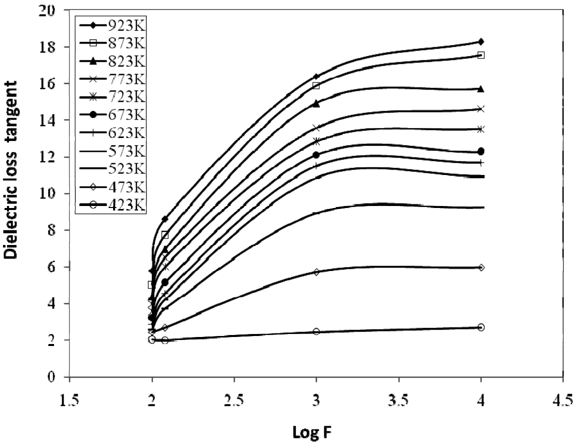

Fig. 8. Variation of dielectric loss tangent (tanδ with frequency of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ at different temperatures.

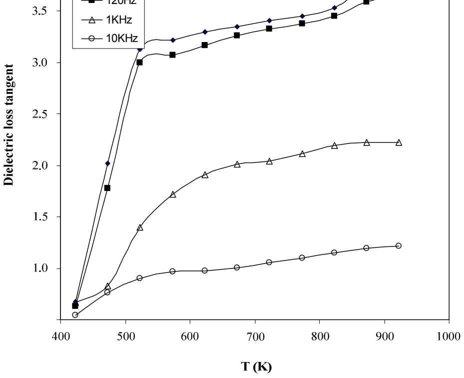

Fig. 9 . Variation of the dielectric loss tangent with temperature of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ at different frequencies.

The variation of dielectric loss tangent (tanδ) with temp is shown in Fig. 9. The dielectric loss tangent (tanδ) shows increase in its values with increasing temperature for all compositions. A typical curve shown is observed for x=0.3.Similar nature was observed in case of other ferrites [21-22].

M. K. Fayek [23] have reported that tanδ versus frequency show a maxima with increasing temperature the maxima shifts towards higher frequency. The frequency range in present series is upto to 10 KHz with which could not reduce the tanδ value and only a present trend in tanδ value could be observed

4. Conclusions

The main results are that Ni-Zn ferrite particle with nano size dimensions are prepared by co-precipitation method. The lattice constant and X-ray density increases with increasing Zn content x. Porosity decreases with Zn content x. The dielectric constant (ε′) decreases with increasing frequency and increases with increasing temperature. Dielectric constant increases with composition upto 0.3 and the decrease with further with further increase in Zn content x. The dielectric loss (ε″) also shown similar nature. The dielectric loss tangent (tanδ) increases with temperature and frequency both.

References

[1] K. Latha, K. S. Mohan, D. Ravinder Phys. Stat Sol (a), **142,** K 103 (1994).
[2] D. Ravinder, K. Latha, J. Appl. Phys. **75**, 6118 (1994).
[3] R. G. Kulkarni, Asian J. Phys. **6,** 204 (1997).
[4] Amarendra K. Singh, T. C. Goel and R. G. Mendiratta, J. Appld. Phys., **91,** 6626 (2002).
[5] Anderson Dias, Nelcy Della Santina Mohallem and Roberto Luiz Moreira J. Phys III, **6**, 843 (1996).
[6] G. Rangmohan, D. Ravinder, A. V. Ramanareddy, B. S. Boyanov, Mat. Lett. **40,** 39 (1999).
[7] R. G. Gupta, R. G. Mendiratta, J. Appl. Phys. **48**, 2998 (1977).
[8] C. Liu, B. Zou, A. J. Rondinone, Z. J. Zhang, J. Phys. Chem. **B 104**, 1141 (2000).
[9] K. M. Jadhav, V. B. Kawade, K. B. Modi, G. K. Bichile, R. G. Kulkarni Physica B **291**, 379 (2000).
[10] A. T. Raghvender, Damir Pajik, Kreso Zhadro, Tomislave Milekovik, E. Vyankateshwar Rao, K. M. Jadhav, D. Ravinder, J. Mag. Mag. Mat. **316**, 1 (2007).
[11] Y. Atassi, M. Tally, J. of Iranian Chem. Soc. **3**, 242 (2006).
[12] P. C. Fannin, S. W. Charles, J. L. Bormann, J. Magn. Magn. Mater **201,** 98 (1999).
[13] Z. Yue, J. Zhou, Lil, H. Zhang and Z Gui, J. Magn. Magn. Mater **208**, 55 (2000).
[14] C. G. Koops, Phys. Rev. **83**, 121 (1951).
[15] L. L. Hench, J. K. West, Principles of Electronics Ceramics, Wiley, New York, 1990, p.189.
[16] Amarendra K. Singh, T. C. Goel, R. G. Mendiratta, O. P. Thakur and Chandra Prakash, J. Appl. Phys. **91,** 6626 (2002).
[17] R. V. Mangalaraja, S. Ananth Kumar, P. Manohar, F. D. Gnanam, Mat. Lett. **57,** 1151 (2003).
[18] A. M. Abdeen, J. Magn. Magn. Mater **192**, 121 (1999).
[19] K. Iwauchi, Jpn. J. Appl. Phys. **10**, 1520 (1971).
[20] V. R. K. Murthy and J. Shobhandri, Phys. Stat. Sol. (a). **36**, 133 (1976).
[21] S. S. Shinde, K. M. Jadhav, Mat. Lett. **37,** 63 (1998).
[22] A. R. Shitre, V. B. Kawade, G. K. Bichile, K. M. Jadhav, Mat. Lett. **56**, 188 (2002).
[23] M. K. Fayek, M. K. Elnimr, F. Sayedahmed, S. S. Ata-Allah, M. Kaiser, Solid State Comm. **115**, 109 (2000).

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