A Study of Microwave Sintered Ni Substituted Lithium Zinc Ferrite Synthesized by Citrate Precursor Method

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Abstract: Li-Zn-Ni ferrite having the compositional formula $Li_{0.4-0.5x}Zn_{0.2}Ni_xFe_{2.4-0.5x}O_4$ where $x=0.02 \leq x \leq 0.1$ in steps of 0.02 was synthesized by the citrate precursor method and pre fired at 650°C in a conventional furnace. It was finally given microwave sintering (MS) at 1040°C. X- ray diffraction pattern confirmed the spinel phase structure. The theoretical and experimental density was calculated. Microstructure of the samples was examined using SEM. Room temperature dc resistivity was measured. Dielectric constant studies was carried out as a function of composition and frequency. Experimental results show resonance in the variation of dielectric loss with frequency. Possible mechanisms contributing to all the above behavior is being discussed.

Key words: Citrate precursor, dielectric constant, ferrites, microwave sintering.

1. Introduction

Lithium and substituted lithium ferrite are important both fundamentally and technologically. Due to their high resistivity and low dielectric loss they are found to be used in several applications like microwave devices, multilayer chip inductor etc. The properties can be tailored by changing different factors like substitution, preparation method, sintering technique etc [1]-[6]. Among various method of preparation, the chemical method such as citrate precursor synthesis of ferrites has attracted the attention of material scientist due to the fact that product with high homogeneity can be obtain. There are many reports dealing with the substitution. The divalent Ni ion is found to increase resistivity and hence lowers the dielectric constant. Also several workers have reported on sintering behavior including grain growth, densification which in turns increase resistivity and their modified forms using microwave heat treatment [7]-[10]. The fast heating rate reducing the processing time in microwave-sintering technique is advantageous to improve various properties like stoichiometry, electrical resistivity etc. Currently an extensive investigation on these microwave properties is being carried out because of their potential applications in microwave devices [11-13]

In view of the importance of microwave sintering, in this work an attempt has been made to synthesize Li-Zn-Ni ferrite by citrate precursor method and sintered using the microwave sintering technique. Further studies are carried out on the dc resistivity and dielectric properties of the microwave sintered samples.

2. Experiment

Nickel substituted lithium zinc ferrites with compositional formula $Li_{0.4-0.5x}Zn_{0.2}Ni_x\ Fe_{2.4-0.5x}O_4$ where $x=0.02 \leq x \leq 0.1$ in steps of 0.02 was prepared by the citrate precursor method. The starting chemicals used

were lithium nitrate, zinc nitrate, iron nitrate, nickel nitrate and citric acid. Stoichiometric amount of lithium nitrate, zinc nitrate, iron nitrate, nickel nitrate and citric acid were mixed to make a solution. The ratio of metal cations to citric acid is 1:1. The solution was mixed homogenously with the help of a magnetic stirrer using a magnetic agitator controlling the pH value at 7. After controlling pH at 7 it was refluxed at 40°C with continuous stirring for about half an hour. The solution was then put in an oven at 100°C forming a dried gel. It get ignited, undergoing a strong auto combustion process with evolution of large amount of gases, giving rise to the ash-synthesized product. The product so obtained is the typical spinel structured lithium zinc nickel ferrite powder. These synthesized powder was mixed with polyvinyl alcohol as binder and pressed into pellets with 50 kilo Newton pressure. It was given a pre firing at 650^{o}C in a programmable conventional furnace for 3 hours with a heating rate of 5^{o}C/min. Finally microwave sintering (MS) at 1040^{0}C was given. The microwave furnace used a single magnetron at 2.45 Ghz frequency at a power output of 1.1 kW. The furnace consists of a Eurotherm temperature controller, a Pt-Rh thermocouple assembly and a susceptor. Spinel phase was confirmed by XRD analysis using X-ray powder diffractometer (Phillips) with CuK_{α} (λ=1.5405 Aº) target and a Ni filter. The lattice parameter and X-Ray density were calculated from the XRD data and their variation with composition studied. Experimental density of the samples was measured using Archimedes' Principle. The particle size was calculated from SEM. Using a precession E4980 LCR meter the capacitance was measured and the value of dielectric constant was calculated using the formula $\varepsilon' = Cd/\varepsilon_0 A$ where C is the measured capacitance, d the thickness, A the cross sectional area of the sample and ε_0 the permittivity of free space. The dielectric constant of the synthesized samples as a function of concentration and frequency (20Hz to 2MHz) were studied. Frequency variation of dielectric loss was also carried out.

3. Results and Discussion

Fig. 1 shows the typical XRD pattern of LiZnNi ferrite(x=0.08). All the XRD peaks identified, confirm the spinel phase structure. No extra peak due to impurities is present.

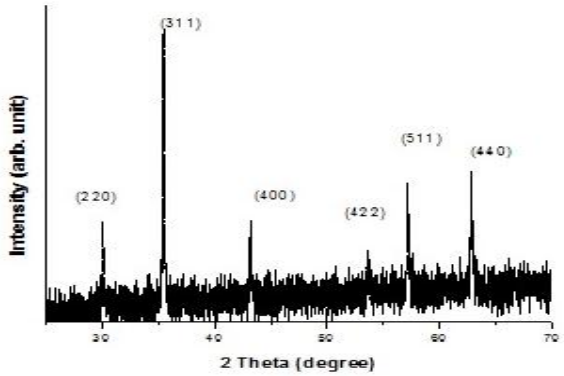

Fig. 1. XRD pattern for $Li_{0.4-0.5x}Zn_{0.2}Ni_xFe_{2.4-0.5x}$(x=0.08)

The lattice constant was calculated from the XRD data of the (311) diffraction peak using the formula $\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$. It showed a decrease with increasing Ni concentration (Table 1). In $Li_{0.4-0.5x}Zn_{0.2}Ni_x\ Fe_{2.4-0.5x}O_4$, since Ni^{2+} ions with ionic radius 0.78 nm substitute Fe^{3+} ions and Li^{1+} ions with radii 0.067nm and 0.078 nm respectively ,the lattice constant is expected to increase. However the decreasing trend is suggestive of the fact that lattice constant does not depend solely on ionic radii and the cationic distribution but may also be influenced by the force acting between the ions like the long range attractive coulomb force, bond length etc. which require further investigation of the existence of surface charge. This is in agreement with the report of other workers [14]-[16]. The densities measured by the Archimedes principle and those calculated from

XRD data are tabulated in Table 1, and an increased is observed with increasing Ni^{2+} concentration. Similar results have been reported by previous workers. The particle size calculated from SEM micrograph show an increasing trend with increasing Ni^{2+} concentration (Table 1). Typical micrograph for x=0.08 is shown in Fig. 2.

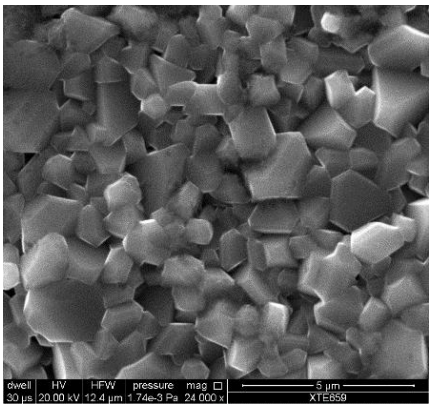

Fig. 2. SEM micrograph for microwave sintered $Li_{0.4-0.5x}Zn_{0.2}Ni_xFe_{2.4-0.5x}$(x=0.08)

Table 1. Lattice Constant, Density-theoretical and Experimental for Microwave Sintered $Li_{0.4-0.5x}Zn_{0.2}Ni_xFe_{2.4-0.5x}O_4$

Conc.	Lattice constant (A^0)	Theo. Density (g/cm^3)	Expt. Density (g/cm^3)	Particle size(nm)
0.02	8.437	4.924	4.184	980
0.04	8.416	4.931	4.306	1090
0.06	8.414	4.936	4.386	1200
0.08	8.402	4.961	4.419	1310
0.1	8.403	5.021	4.491	1500

Fig. 3 shows the dependence of d.c. resistivity with Ni^{2+} concentration. It can be understood from the cationic formula which can be written as, $(Zn_{0.2}Fe_{0.8})[Li_{0.4-0.5x}Ni_xFe_{1.6-0.5x}]O_4$,

According to the cationic formula, the number of Fe^{3+} ions at B site decreases with the increase in Ni^{2+} ion content. As the dominant conduction mechanism in ferrites is the hopping of electrons between Fe^{2+} and Fe^{3+} ions on the B sites, the observed increase in resistivity is expected.

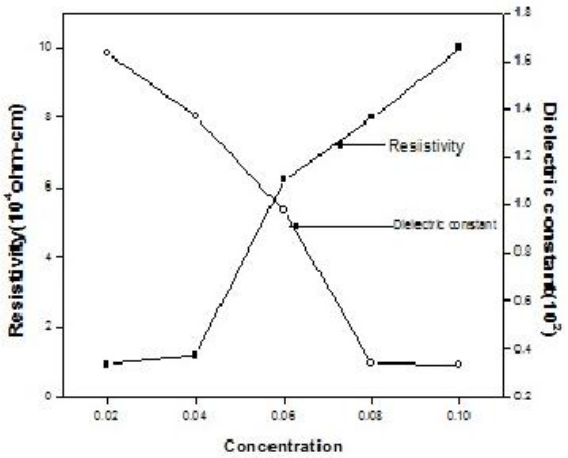

Fig. 3. Variation of dc resistivity and dielectric constant with concentration for $Li_{0.4-0.5x}Zn_{0.2}Ni_xFe_{2.4-0.5x}$

The compositional variation of room temperature dielectric constant of the ferrite samples at 10 KHz

depicted in Fig. 3 shows a decrease. The variation can be explained on the basis of space charge polarization and Koop's two layer model, where the ferrite is assumed to be made up of well conducting grains separated by poor conducting layers or grain boundaries. The electrical conduction in ferrite can be explained by the Verwey mechanism of electron hopping, where conduction takes place through hopping of electrons between Fe^{2+} and Fe^{3+} ions at B sites[17]-[18]. The electrons, by hopping, reach the grain boundary and due to the high resistivity of the grain boundary get piled up, thereby producing space charge polarization. The substitution of Ni^{2+} ions decreases the Fe^{3+} ion at the B sites according to the cationic formula, $(Zn_{0.2}Fe_{0.8})[Li_{0.4-0.5x}Ni_xFe_{1.6-0.5x}]O_4$, produces a change in the polarization thereby decreasing the hopping motion of electrons. This in turn impedes the build up of space charge. The value of dielectric constant therefore decreases.

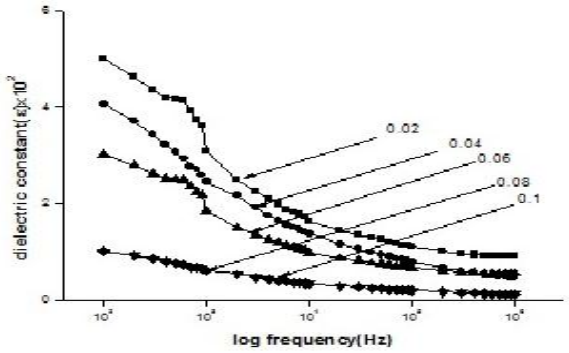

Fig. 4. Variation of dielectric constant with frequency for $Li_{0.4-0.5x}Zn_{0.2}Ni_xFe_{2.4-0.5x}$

Fig. 4 shows the frequency dependence of dielectric constant for all the samples. The dielectric constant is observed to show dispersion in the frequency range under investigation, its value being high at low frequencies, and then decreases rapidly with increase in frequency. At a much higher frequency the dielectric constant is low and remains almost constant. Similar observation has been reported by other workers. The observed dispersion can be explained in terms of the space charge polarization and Koop's two layer model as has been mentioned before. As the frequency of applied field is increased the electronic exchange is not able to follow the alternating field as the electrons reverse the direction of motion. The polarization therefore decreases and hence the observed decrease in dielectric constant. At still higher frequency, the polarisability is very small and becomes frequency independent.

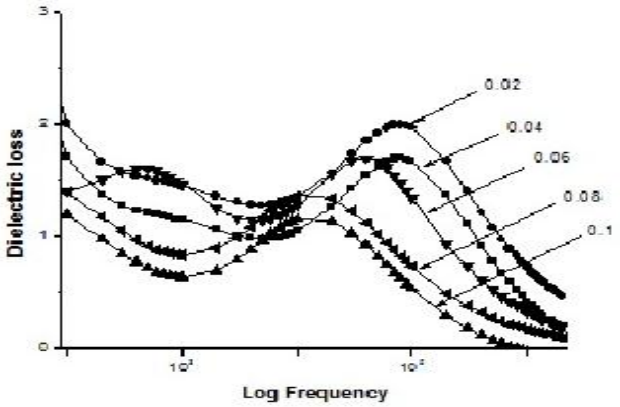

Fig. 5. Variation of dielectric loss with frequency for $Li_{0.4-0.5x}Zn_{0.2}Ni_xFe_{2.4-0.5x}$

The plot of loss tangent as a function of frequency is depicted in Fig. 5. The appearance of a resonance peak at higher frequency can be explained in terms of the matching of the hopping frequency with

externally applied field. Since the dielectric behaviour of ferrites is attributed to the electron hopping between Fe^{3+} ion and Fe^{2+} ion, the probability of jumping of ions from Fe^{3+} ion to Fe^{2+} ion and Fe^{2+} ion to Fe^{3+} ion are same. Depending upon this probability, the ion exchange position between the two states at frequency called natural frequency of jump for the two positions. If the frequency of applied field is the same as the natural frequency, the maximum electrical energy is transferred to the oscillating ions and power loss shoots up resulting in a resonance [18-20]. It was reported that higher heat treatment lowers the resonance peak and also higher heat treatment gives more densification [19]. In the present study the substitution of Ni^{2+} gives more densification which may be related in lowering the resonance peak. However a detail investigation needs to be carried out.

4. Conclusions

Ni substituted lithium ferrite was prepared by citrate precursor method. The increase in the substitution of Ni^{2+} gives more densification, increases room temperature dc resistivity while it decreases the dielectric constant. Dispersion behavior is observed for the variation of dielectric constant with frequency where high dielectric constant is observed at low frequency and decreases with the increase in the frequency. Resonance phenomena is observed for dielectric loss variation with frequency for all samples. However the change in the resonance peak may be effect of Ni^{2+} substitution such that with increase in Ni^{2+} substitution there is a lowering of resonance peak. Further investigation needs to be explored such that the observed properties can be used for specific application.

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References

[1] Amarendra, K. S., Goel, T. C., Mendiratta, R. G., Thakur, O. P., & Chandra, P. (2002). Dielectric properties of Mn-substituted Ni–Zn ferrites. *J. Appl. Phys*. *91, 6626.*

[2] Amarendra, K. S., Verma, A., Thakur, O. P., Chandra P., Goel, T. C., & Mendiratta, R. G. (2003). Electrical and magnetic properties of Mn-Ni-Zn ferrites processed by citrate precursor method. *Mater. Lett. 57, 1040.*

[3] Ibetombi S., Sumitra P., & Chandra P. (2009). Mössbauer and magnetic studies of cobalt substituted lithium zinc ferrites prepared by citrate precursor method. *J. Alloys Compounds*, *475, 328.*

[4] Soibam, I., Phanjoubam, S., Sarma, H. N. K., & Chandra P. (2008). Synthesis and characterization of ultra-fine zinc substituted lithium ferrites. *AIP Conf. Proc*. *1003, 136.*

[5] Ibetombi S., Sumitra P., Sharma, H. B., & Sarma, H. N. K. (2008). Synthesis of lithium zinc ferrite powders by citrate precursor gel formation method. *Indian J. Phys*. *82, 611*.

[6] Ahmed, M. A., Darwish, K. A., & EL-Khawas, E. H. (1997). Heating rate effect on the electrical properties of Mn_xZn_{1-x} Fe_2O_4 ferrite (x=0.28, 0.48, 0.64, 0.76). *Journal of Materials Science Letters. 16, 1948.*

[7] Martha, P. (2000). Microwave applications of soft ferrites. *Journal of Magnetism and Magnetic Materials. 216, 171.*

[8] Cheng-Hsing, H., & Chia-Hao, C. (2012). Microwave dielectric properties of new (Ca 0.8 Sr 0.2) SnO 3 ceramics. *Ceramics International, 38, 4411.*

[9] Morteza, O., & Omid, M. (2010) Microwave versus conventional sintering: A review of fundamentals, advantages and applications. *Journal of Alloys and Compounds. 494, 175–189.*

[10] Muhammad, N. A., Nasreen, B., & Muhammad, A. M. (2010). Effect of Sn–Ni substitution on the structural, electrical and magnetic properties of mixed spinel ferrites. *J. Alloys Compounds, 594.*

[11] Yang, Q. H., Zhang, H. W., Liu, Y. L., Wen, Q. Y., & Jia L. J. (2012). Microstructure and magnetic properties of microwave sintered NiCuZn ferrite for application in LTCC devices. *Materials Letters.* 79, 103.

[12] Shannigrahi, S. R., Pramoda, K. P., & Nugroho, F. A. A. (2012). Synthesis and characterizations of microwave sintered ferrite powders and their composite films for practical applications. *Journal of Magnetism and Magnetic Materials*, *324*, 140

[13] Cheng-Hsing H., & Chia-Hao C. (2012). Microwave dielectric properties of new (Ca0.8Sr0.2)SnO3 ceramics. *Ceramics International,* 38, 4411.

[14] Smit, J., & Wijn, H. P. J. (1959). *Ferrites*. Philips Technical Library, Eindhoven.

[15] Sattar, A. A., El-Sayed, H. M., Agami, W. R., & Ghani, A. A. (2007). Magnetic properties and electrical resistivity of Zr4+ substituted Li-Zn ferrite. *Am. J. Appl. Sci*., *4*, 89.

[16] Brian, T. N., & David, R. C. Lattice expansion and saturation magnetization of Nickel–Zinc ferrite nanoparticles prepared by aqueous precipitation. *J. Am. Ceram. Soc*., *90*, 3541.

[17] Koops, C. G. (1951). On the dispersion of resistivity and dielectric constant of some semiconductors at audiofrequencies. *Phys. Rev*. *83,* 121.

[18] Verwey, E. J. W., Haayman, P. W., & Romeijn, F. C. (1947). Physical properties and cation arrangement of oxides with spinel structures II. Electronic Conductivity. *J. Chem. Phys*. *15,* 181.

[19] Hench, L. L., & West, J. K. (1990). *Principles of Electronics Ceramics*, John Wiley and Sons, New York, 189.

[20] Chongtham, S., Phanjoubam, S., Sarma, H. N. K., Laishram, R., & Prakash, C. (2005). Dielectric Properties of Li-Sb Ferrites. *Modern Phys. Lett. B*, *19,* 899.

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