Structural and Magnetic study of single and double sintered Li-Ni ferrite

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Abstract— Polycrystalline Ni substituted lithium ferrite $Li_{0.5-0.5x}$ Ni_x $Fe_{2.5-0.5x}$ O_4 where $0.1 \leq x \leq 0.5$ in steps of 0.1 have been synthesized by citrate precursor method. A series of samples were given single sintering (SS) and another series double sintering (DS). Various technique such as X-ray powder diffraction (XRD) for structural study, LCR meter for complex permeability and BH loop tracer for magnetisation were used to carry out the comparative study. Comparing the SS and DS samples SS samples shows higher value of initial permeability and saturation magnetization. For both the series variation of initial permeability as a function of frequency shows decrease. The variation in the results obtained for SS and DS samples along with the mechanism involved are discussed.

Keywords: Citrate Precursor, XRD, Permeability, Saturation magnetization

I. INTRODUCTION

Spinel ferrites have excellent electrical and magnetic properties like high resistivity, low eddy current losses, high saturation magnetization, high curie temperature and large permeability at high frequency which makes them suitable for a wide range of applications such as phase shifter, magnetic core, microwave absorbers, medical diagnostics, radio frequency circuits, transformer cores, magnetic resonance imaging (MRI) and magnetic drug-delivery technology etc. [1-3]. For the present investigation, Ni substituted lithium ferrites have been synthesized using low temperature synthesis method known as the citrate precursor method. This synthesis method has been reported as a versatile method for obtaining nano crystalline ferrite particles, as low temperature is used. It allows homogeneous distribution of ions at the atomic level, good control of stoichiometry, small particle size formation and high efficiency. Besides, it is simple, inexpensive and less time consuming. However it is learnt that densification, grain growth, magnetic and electrical properties etc. were affected by sintering phenomena. Lack of reports on a systematic investigation of the comparison of structural, magnetic and electrical properties of substituted ferrites sintered using single and double sintering techniques have prompted the present study.

Therefore, in the present work, Ni substituted lithium ferrite was prepared by citrate precursor method. Further, a comparative study on the properties such as structural and magnetic properties of Li Ni ferrites sintered using single and double sintering is carried out.

II. EXPERIMENTAL DETAILS

$Li_{0.5-0.5x}$ Ni_x $Fe_{2.5-0.5x}$ O_4 where $0.1 \leq x \leq 0.5$ in steps of 0.1 were synthesized by the citrate precursor method using Lithium nitrate $LiNO_3$ (Merck, Germany); Nickel (II) nitrate hexahydrate $Ni(NO_3)_2.6H_2O$ (Merck, India); Iron (III) nitrate monohydrates $Fe(NO_3)_3.9H_2O$ (Merck, India); and citric acid monohydrates $C_6H_8O_7$ (Merck, India). The preparation method is discussed elsewhere [4]. The samples were then mixed with polyvinyl alcohol (PVA) as a binder and pressed to form pellets (10mm diameter) and toroidal rings (30mm outer diameter, 10mm inner diameter and 4mm thickness) by applying a pressure of 10 ton cm^{-2}. These samples were given sintering, single sintering (SS) for one series at a temperature of 1040°C and for another series double sintering (DS) was given (pre sintering at 650°C followed by second sintering at 1040°C). The sintered pellets were coated with silver paste to provide electrical contact and the toroidal rings were wounded with 70 turns of 30 SWG enamelled copper wire. The phase identification and structure analysis of the sintered samples were performed using Philips X-ray diffractometer (SS and DS) with CuKα radiation (λ= 1.5406Å).From the XRD data the lattice constant, density, and the crystallite size(Debye-Scherrer relation) of each composition was determined. Complex initial permeability as a function of composition, frequency (20Hz- 2MHz) and sintering types (SS, DS) were carried out. Inductance (L) and the corresponding loss factor tanδ of the sintered toroids were measured in the frequency range of 20Hz – 2MHz using a precision LCR meter E4980A. The measured inductance was used to calculate the initial permeability given as ,

$$\mu_i' = \frac{L}{L_o} = \frac{L}{4.6N^2 \times \log\frac{OD}{ID} \times h \times 10^{-9}}$$

where L is the measured inductance, L_o is the air core inductance , N is the number of turns of the coil (N=70), h is the thickness, OD is the outer diameter and ID is the inner diameter of the toroidal specimen. Saturation magnetization (M_s) was determined from B-H hysteresis loops measured by B-H loop tracer (Ferrites India) working on 50 Hz mains frequency.

III. RESULTS AND DISCUSSION

Typical X-ray diffraction (XRD) patterns of x=0.1 [Fig.1 (a) SS, 1(b) DS] of Ni substituted lithium ferrites can be well indexed to standard JCPDS card thereby confirming the formation of single phase cubic spinel structure. The patterns showed the absence of impurity phase.

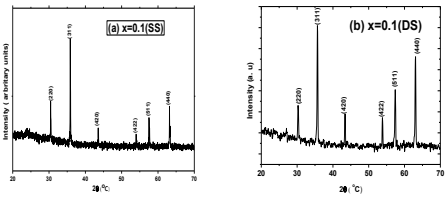

FIGURE 1 XRD patterns of the Li Ni ferrites for (a) SS and (b) DS

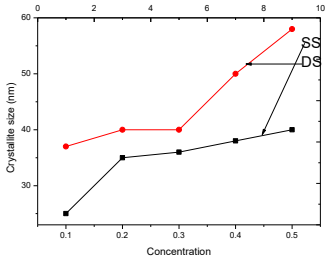

FIGURE 2 Crystallite size with concentration for SS and DS

The XRD parameters like lattice constant, X-ray density and crystallite size were tabulated in Table 1. Lattice expansion occurs if the doping ion has larger radii than the displaced ion. In the present investigation, Ni^{2+}ions of ionic radius 0.69Å substitute Li^{1+} (0.74) and Fe^{3+} (0.067) respectively. However there is no observable effect for SS and DS samples in the present study.

TABLE 1: Lattice parameter, X-ray density, experimental density, and porosity of Li $_{0.5-0.5\,x}$ Ni_x $Fe_{2.5-0.5x}O_4$ ferrites.

Conc.	Lattice constant [nm]		Theo. Density [g/cm³)]		Expt. Density [g/cm³]		Porosity %	
	SS	DS	SS	DS	SS	DS	SS	DS
0.1	0.84	0.83	4.68	4.80	3.74	4.10	20	17
0.2	0.83	0.83	4.86	4.86	4.14	4.29	14	12
0.3	0.83	0.83	4.89	4.89	4.26	4.38	12	11
0.4	0.83	0.82	5.06	5.07	4.45	4.59	12	9
0.5	0.82	0.82	5.14	5.15	4.57	4.94	11	5

An increasing trend in density (theoretical and experimental) was observed with increase in Ni^{2+} ion concentration. This can be explained on the basis that atomic weight of Ni^{2+} (58.71 amu) is greater than atomic weight of Li^{1+} (58.69amu) and Fe^{3+} (58.84amu).The increase in density with Ni^{2+} ion substitution may be attributed to the acceleration of cation interdiffusion due to Ni^{2+} ion and increase in reactivity of the fine ferrite grains which coalesce to form bigger grains resulting in pore reduction and volume shrinkage. On the one hand the crystallite sizes increases with increasing Ni^{2+} ion concentration.

In case of the two types of sintering, the density is greater for the DS samples than that of the SS samples. This could be due to longer exposure to sintering for the DS sintered samples. During sintering process, the thermal energy generates a force which drive grain boundaries to grow over pores reducing the porosity and hence densifying the material which in turn leads to increase crystallite size. The average crystallite size[Fig.2] of all the samples are found to be in the range 25nm-40nm for SS samples and 37nm-58nm for DS samples clearly indicating that higher densification correspond to greater crystallite size in the present study[5-7].

Complex initial permeability represented as

$\mu = \mu_i' - j\mu_i''$

where μ_i' is the real part of initial permeability known as initial permeability and μ_i'' is imaginary part of initial permeability known as the permeability loss was investigated. The real part of complex permeability decreases with increasing Ni^{2+} ion concentration[Fig.3]. According to Globus permeability occurs due to domain wall motion [8]. So with higher Ni^{2+} ion concentration there is decrease number of pores within the grains. The pore act as pinning site for domain wall movement restricting the movement and hence decreases the permeability. Also it has a linear relationship existing between grain diameters such that, as the diameter increases the density increases reducing the magneto crystalline anisotropy and hence decreases the internal stress. Therefore the hindrance given to movement of domain walls decrease with the results that initial permeability increases. In the present investigation there is an increase in grain size with decrease porosity such that increase in initial permeability is expected which was observed. However initial permeability is considered to be an interplay of various parameters like composition, porosity, density, microstructure, saturation magnetisation etc.[5, 9].

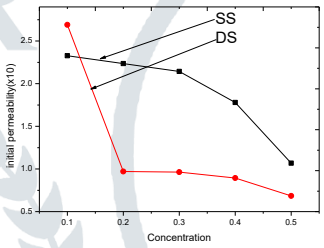

FIGURE3: Initial permeability of SS and DS

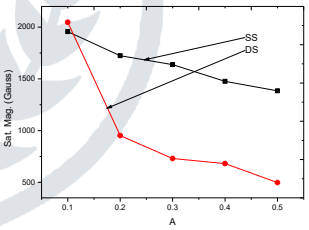

FIGURE4: Saturation magnetisation of SS and DS

To support the decrease permeability in the present case, investigation on the value of saturation magnetisation as a function of Ni^{2+} ion concentration is carried out using BH loop tracer. A typical hysteresis loop for x=0.5 for SS and DS sample is shown in Fig. 5. The variation of Ms values with Ni^{2+}ion content is shown in Fig. 4. According to Neel's model the net magnetisation is the vector sum of magnetisation of two sub lattice, $\mathbf{M=M_B-M_A}$ where $\mathbf{M_A}$ and $\mathbf{M_B}$ are magnetisation of sub lattice A and B respectively. In the present ferrite samples Ni^{2+} ions have strong preference for the B site and Fe^{3+} ions partially occupy the A and B sites. The resultant magnetization, M is the difference of the magnetizations $\boldsymbol{M_B}$ and $\boldsymbol{M_A}$ of the B and A sublattices respectively. The cation distribution can be written as $(Fe)\,[Li_{0.5x-0.5x}Ni_xFe_{1.5-0.5x}]O_4^{2-}$ where parenthesis and square bracket represent tetrahedral (A) and octahedral (B) sites respectively. As Li^{1+} is non-magnetic it doesn't contribute so, Ni^{2+} and Fe^{3+} only gives effect on net magnetisation. The magnetic moment of $Ni^{2+}$is $2\mu_B$ and that of Fe^{3+} is $5\mu_B$, therefore, the net magnetisation becomes (2x+7.5-2.5x)-5 =2.5-0.5x. Consequently, M_s values will

decrease with increasing Ni^{2+} ion substitution and was observed experimentally. The decrease in saturation magnetisation possibly explain up to some extent the decrease in initial permeability according to the relation $\mu_i' = \frac{M_s D}{\sqrt{k}}$ where M_s is the saturation magnetization, D is the grain size, and K is the anisotropy constant [10]. Considering SS and DS the values of initial permeability are higher in DS samples. This may be due to higher densification, lesser pores as was explained above. Considering the SS and DS for saturation magnetisation it is found that DS is lower than SS.

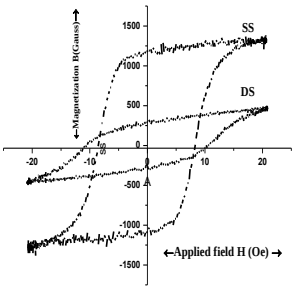

FIGURE5: BH loop of SS and DS

The plot of real part of initial permeability, μ_i' vs frequency for all the toroids prepared by SS and DS techniques are shown in Fig. 6(a) SS, 4(b) DS. For both series dispersion is observed at low frequency and at higher frequency the value of initial permeability decreases. At still higher frequency, it is independent of frequency. At low frequency the domain oriented in the direction of applied field grows at the expense of its neighbour which is oriented in different direction. At higher frequency the direction of domain wall is not able to move sufficiently rapidly to follow the alternating field. The overall magnetization vector does not follow the applied field hence produce a low value of initial permeability.

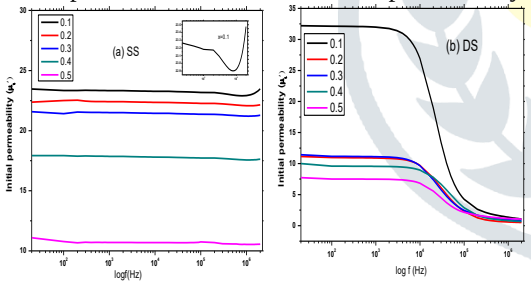

FIGURE 6 Initial permeability vs frequency for (a) SS and (b)DS samples

IV. CONCLUSION

Addition of Ni^{2+} ion increases densification and crystallite size while porosity decreases. Experimental results shows differences on the various properties of single sintered (SS) and double sintered (DS) Li Ni ferrites. DS samples show higher densification than SS samples due to longer exposure of sintering and in the process thermal energy might have been generated force which drives the grain boundaries to grow over pores reducing porosity which increases density and further the crystallite size. Higher value of initial permeability in SS samples compared to DS samples was observed and it was explain based on the decrease of pore growth giving less hindrance to domain wall motion and hence increases the value. It was also supported by study of saturation magnetisation. The initial permeability has a direct relation with saturation magnetisation which is higher in SS samples and so does the initial permeability. The higher value of saturation magnetisation in SS samples maybe due to the higher grain size.

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