Dielectric Studies Of Li-Ni Ferrite Prepared By The Citrate Precursor Method

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Abstract

Ni substituted Li ferrites with compositional formula $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$ where $0.1 \leq x \leq 0.5$ in steps of 0.1 was synthesized by using citrate precursor method. The sample was given final sintering at 1040^oC after a pre-sintering at 650^oC. X-ray diffraction was used to confirm the spinel phase. From the analysis of the XRD data the lattice parameter, theoretical density, porosity and crystallite size was calculated. The surface morphology of the samples was studied by using scanning electron microscopy (SEM). Room temperature dc resistivity and dielectric constant at 10 kHz were investigated. The dc resistivity showed an increased while the dielectric constant decreased with addition of Ni^{2+} ions. It was explained in terms of space charge polarization and koops two layer model. The variation in dielectric constant with frequency showed dispersion. Possible mechanism responsible for the above behavior is being discussed.

Keywords: Ferrites, Citrate precursor, XRD, SEM, Dielectric constant.

1.   Introduction

Ferrites had been studied by many workers because of their varied technological applications [1-5]. They are found to be used in military devices, power transformer in electronics and devices at radio frequencies due to their characteristic dielectric properties [6-9]. The properties of ferrites depend upon various factors like the synthesis method, type of substitutions and the sintering temperature [10-11]. It is generally accepted that lithium, probably as the oxide, volatilizes rapidly from lithium ferrite at high temperature. In order to avoid this, synthesis of lithium ferrite at low temperature is preferred. Citrate precursor method is a particular type of synthesis method which gives ferrite at low temperature [12]. Also, in ferrites the cations

occupy the tetrahedral (A) and octahedral (B) sites and the compositional variation due to substitution results in the redistribution of metal ions over the tetrahedral and octahedral sites. This gives a modification in the dielectric properties of ferrite [10, 13]. The study of dielectric behavior with respect to frequency gives valuable information regarding localized charge carrier and dielectric polarization.

In the present work; investigation of the dielectric properties of citrate precursor prepared Ni substituted lithium ferrites as a function of composition and frequency is undertaken.

2.   Experiment:

Nickel substituted lithium ferrite with the formula $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$ was synthesized by the citrate precursor method. The starting chemicals used were analytical grade lithium nitrate, nickel nitrate, iron nitrate and citric acid. Stoichiometric amount of lithium nitrate, nickel nitrate, iron nitrate and citric acid were mixed to make a solution. The ratio of metal cations to citric acid is 1:1. The synthesis method is discussed elsewhere [14]. The synthesized powder was mixed with a binder and pressed into pellets with 50 kilo Newton pressure. The samples were pre-sintered at 650^OC followed by a final sintering in air at 1040^OC. From the XRD data the lattice parameter, theoretical density, porosity and crystallite size was calculated for all the samples. Scanning electron microscopy (SEM) micrograph was recorded using FEI quanta 250. Dielectric constant at room temperature was studied as a function of composition and frequency (20Hz-1MHz) for all samples. The measurement was carried out using an Agilent E4980A Precision LCR meter and the value of dielectric constant was calculated using the formula $\varepsilon^{'} = \dfrac{Cd}{\varepsilon_0 A}$ 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.

3.   Results and Discussion

XRD pattern was used to confirm the spinel phase structure of the prepared sample. All the peaks could be indexed to the standard pattern reported by the Joint Committee on Powder Diffraction Standards (JCPDS). There is no extra peak observed showing that there is no impurity present. A typical XRD for concentration of Ni=0.1 and Ni=0.5 is shown in Fig.1(a) and Fig.1(b).
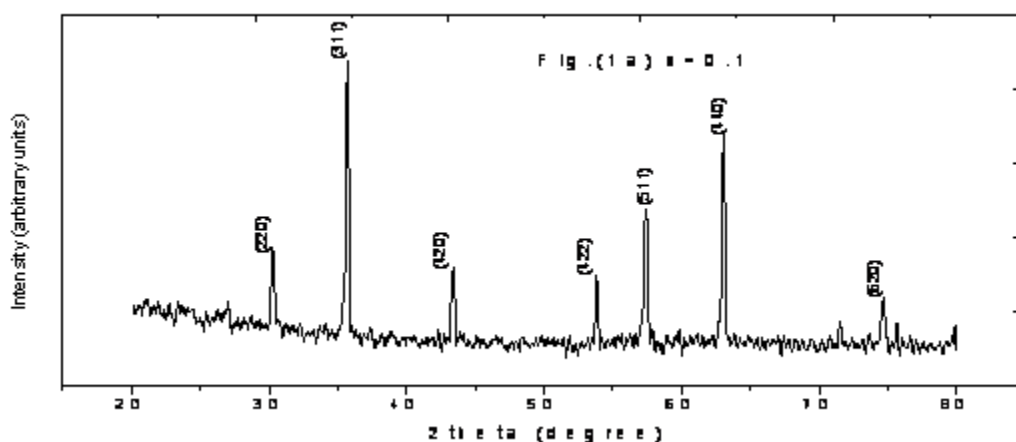
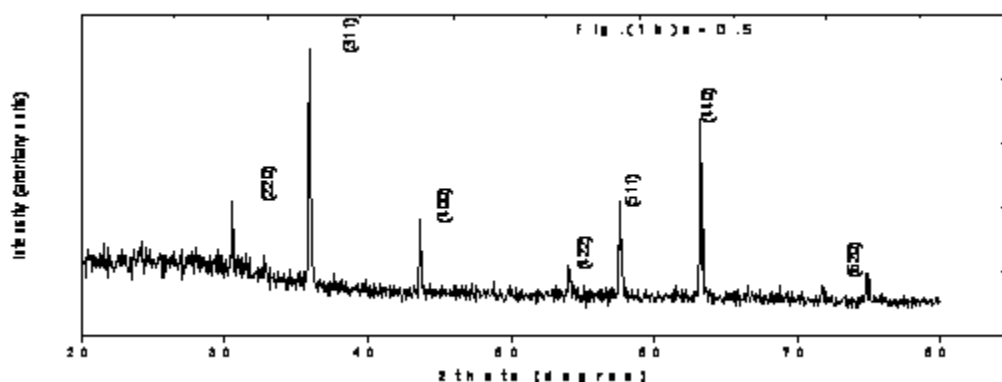**Fig. 1(a) X-ray diffraction patterns of $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$, x=0.1**

Fig. 1(b) X-ray diffraction patterns of $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$, (b) x=0.5

The lattice parameter, theoretical densities and crystallite size of the samples calculated from the XRD data was tabulated in Table 1. From the XRD data the lattice parameter 'a' was calculated and a decrease is observed with the increase in Ni^{2+} ion concentration (Table1). The lattice expansion takes place if the doping ion has larger radii than the displaced ion. In the present series of ferrite samples Ni^{2+} ion with ionic radius 0.078 nm substitute Fe^{3+} and Li^{1+} ions with radii 0.067nm and 0.078 nm respectively, and the lattice parameter is expected to decrease and was observed[10].

The densities of the samples calculated from the XRD data and those measured experimentally using the relation mass per volume are tabulated in Table 1. Both the densities were observed to increase with the increase in Ni ion concentration. These results are in agreement with the observations by previous workers [10,15]. The

porosity has been calculated using the formula $P(\%) = \dfrac{\rho_{theo} - \rho_{expt}}{\rho_{theo}}$ where ρ_{theo} is theoretical or XRD density, ρ_{expt} is experimental density and is in the range of 5%-18% . It shows a decreasing trend with increased in the Ni concentration. It is expected that there is shrinking of pores with increase in the densification. The crystallite size is calculated from XRD data using Debye Scherrer formula which is given as crystallite size$=0.9\lambda/\beta\cos\theta$ where λ is wavelength, β is full width at half maximum. It shows an increasing trend with increase in Ni concentration. This is because the average crystallite size increases slowly with densification [16].

Table1. Lattice parameter, Density (theoretical & experimental), porosity and crystallite size of $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$

Conc.	Lattice parameter (A°)	Theoretical density(gm/cm³)	Experimental density (gm/cm³)	Porosity (%)	Crystallite size(nm)
0.1	8.378	4.8052	4.0015	17	37
0.2	8.339	4.8614	4.2945	12	40
0.3	8.323	4.8949	4.3869	10	40
0.4	8.294	5.0740	4.5995	9	50
0.5	8.284	5.1571	4.9465	5	58

The SEM micrograph [Fig. 2(a) –Fig. 2(b)] shows an increasing growth of particle with increase in the Ni ion concentration. This is because the increase in density increases slowly the particle size.
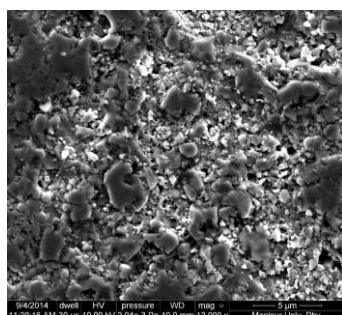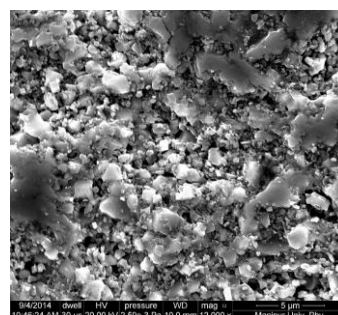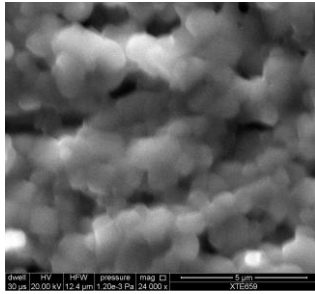

Fig. (2a) x=0.1   **Fig. (2b) x=0.2**
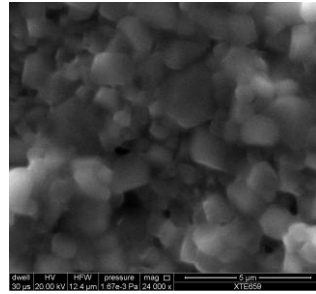
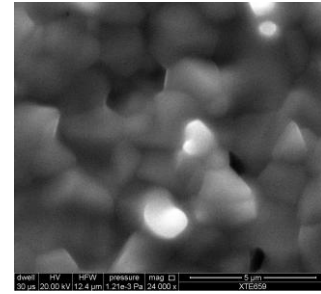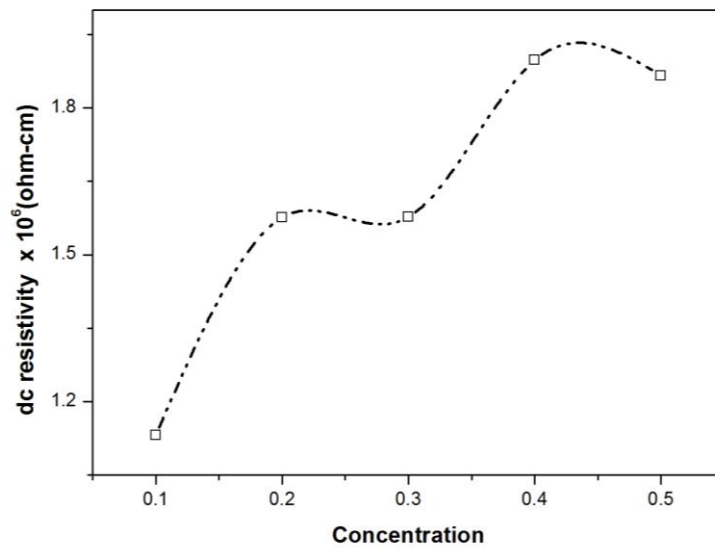**Fig. (2c) x=0.3**   **Fig. (2d) x=0.4**   **Fig. (2e) x=0.5**

Fig. 2. SEM micrograph for $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$

The variation of dc resistivity (Fig.3) and room temperature dielectric constant measured at 10 kHz (Fig.4) is studied. It is observed that the resistivity increases while the dielectric constant decreases with the increase in the addition of Ni^{2+} ions.

Fig.3. Variation of dc resistivity with Ni concentration for $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$ (10 kHz).
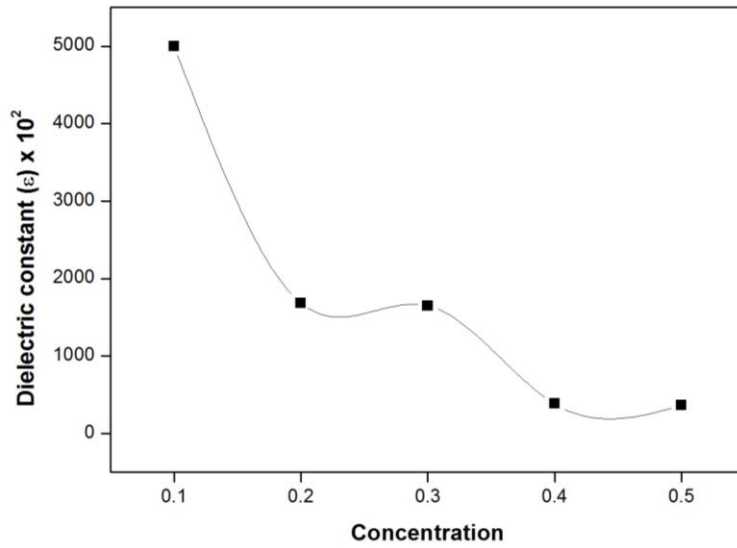
Fig.4. Variation of r.t dielectric constant with Ni concentration for $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$ (10 kHz).

The decrease in the dielectric constant can be explained on the basis of space charge polarization and Koop's two layer model [17]. According to the model, ferrite is assumed to be made up of well conducting grains separated by grain boundaries. The electrical conduction in ferrite is explained by Verwey mechanism in terms of the hopping of electrons between Fe^{2+} and Fe^{3+} ions at B sites [18,19]. The electrons reach the grain boundary by hopping and pile up due to its higher resistivity. This produces the space charge polarization. In the present study, the substitution with Ni^{2+} ions produces a change in the polarization so developed, as can be understood by considering the cationic formula, $(Fe)[Li_{0.5-0.5x}Ni_xFe_{1.5-0.5x}]O_4$. There is a decrease in Fe^{3+} ions and increase in Ni^{2+} ions at the B site as Ni content is increased. However, compared to $Fe^{2+} \rightarrow Fe^{3+}$, the exchange process of $Ni^{2+} \rightarrow Ni^{3+}$ is weak. Hence $Fe^{3+} \rightarrow Fe^{2+}$ is assumed to be the dominant mechanism [10]. The decrease in Fe^{3+} ion at the B site therefore decreases the hopping motion of electrons. This in turn decreases the piling up of electrons at the grain boundary, hence impeding the buildup of space charge polarization. The value of dielectric constant therefore decreases.

The frequency dependence of dielectric constant is shown in Fig. 5. It is observed that the dielectric constant shows dispersion with increasing frequency which is a normal behavior of ferrites. The value of dielectric constant is high at low frequencies but decreases rapidly with increase in the frequency. The observed decrease in dielectric constant with frequency can be explained in terms of the space charge polarization and Koop's two layer model as has been mentioned above [17]. At low frequency of applied field the high resistivity grain boundary hinders the hopping motion of electrons creating space charge polarization, leading to a high dielectric

constant. As the frequency of the applied field is increased the electronic exchange is not able to follow the alternating field and the electrons reverse the direction of motion thus decreasing the probability of electrons reaching the grain boundary. This leads to a decrease in the value of dielectric constant. At still higher frequency, the polarisability is very small and becomes independent of frequency.
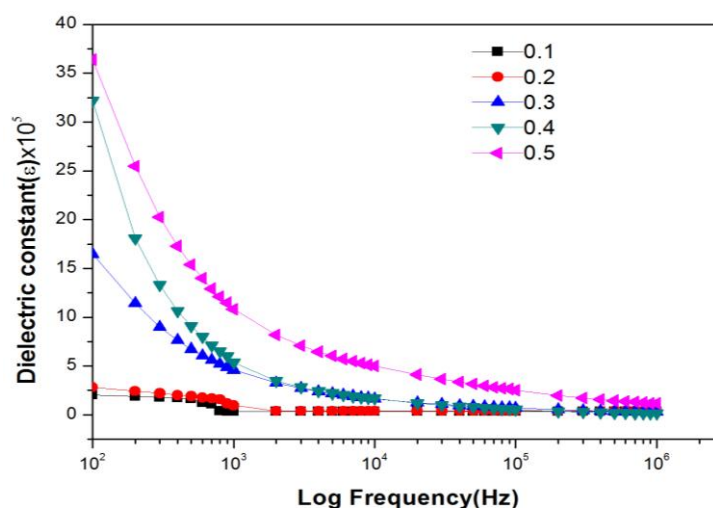

Fig.5. Dielectric constant variation with frequency for $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$

4.   Conclusions

Ni substituted lithium ferrite has been prepared by citrate precursor method. The increase in the substitution of Ni concentration increases the crystallite sizes giving more densification while the lattice parameter and porosity decreases. Dielectric constant is observed to decrease whereas dc resistivity increases with the addition of Ni^{2+} ions. Dispersion behavior is observed for the variation of dielectric constant with frequency. The dielectric constant is high at low frequency and decreases with the increase in the frequency.

Acknowledgement

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