Sintering Effect on the Structural and Electrical Properties of Li$_{0.4}$Ni$_{0.2}$Fe$_{2.4}$O$_4$ Prepared by Citrate Precursor Method

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Abstract

Ferrite having the composition Li$_{0.4}$Ni$_{0.2}$Fe$_{2.5}$O$_4$was prepared by the citrate precursor method.In this method redox reaction takes places giving the ash prepared (AP) product. The AP samples was given sintering one using conventional sintering (CS) technique and another using microwave sintering(MS) technique at a temperature of 500°C. XRD patterns and FTIR spectra confirmed the formation of spinel phase structure.It is observed that sintered samples show higher densification and reduced porosity as compared to AP samples. The crystallite size of all samples was found to be in the range of 20-25nm. FTIR analysis shows the existence of two strong absorption bands which corresponds to Fe-O stretching of tetrahedral and octahedral sites.Another weak band corresponding to Li-O stretching is also observed. Electrical studies such as dielectric constant, dielectric loss, dc resistivity were carried out.Dielectric constant and dielectric loss were studied as a function of frequency for the AP and sintered samples. Experimental results show dispersion for both dielectric constant and dielectric loss. It is also observed that the value of dielectric constant for sintered samples is lower than that of AP samples. This may be attributed to the suppression of electronic exchange between ions. A low dielectric loss is observed in sintered samples as compared to AP samples and lowest value of losses is found in MS samples. DC resistivity is highest in MS samples and lowest in AP samples. The possible reason for all the above observed results is being discussed.

INTRODUCTION

Spinel ferrites is one of the important ferrimagnetic material which have been widely used in various technological applications due to their characteristics structural, electrical and magnetic properties[1-3]. For tailoring the properties of the lithium based ferrites, attempt can be made by varying synthesis methods, substitutions, controlling sintering temperature, sintering techniques etc. It is learnt that synthesis of lithium based ferrites material require low temperature in order to avoid the volatilization of lithium and oxygen. Hence citrate precursor synthesis method which used low temperature is employed in the present study. Moreover the method is simple, easy and economic as compared to other method.

Substitution of common substituent ion such as Ni^{2+},Cu^{2+},Cd$^{2+,}$ Zn^{2+} etc. affects the properties of the lithium ferrites. It is reported that a small amount of Ni ion substitution in the basic lithium ferrite improved densification, increases electrical resistivity and decreases dielectric constant. Besides it also helped to reduce power loss which makes them useful for power application [4]. Considering sintering temperature, optimum sintering temperature is essential as it control almost all the properties. It also influences many properties such as mechanical strength, electrical properties etc. [5]. Also the properties is being affected by sintering technique. There are several sintering techniques of which conventional sintering technique is frequently used. Although it is used by several workers it offers some disadvantages such as longer sintering time to complete the reaction process which consumes more energy. In order to minimize time and energy microwave sintering technique is used. In microwave sintering technique, heat is generated internally within the sample with fast heating rate and it is heated by conversion of electromagnetic energy into heat instead of transferring thermal energy from external sources which happens in a conventional sintering technique [6]. Microwave sintering technique has the advantage of reducing the material losses during sintering. Thus the effect of sintering on different properties emerges as a hot topic and becomes an area of great investigation.

In the present work, an attempt has been made to synthesize Li Ni ferrite by the citrate precursor method. It was given sintering by two techniques, the conventional sintering and the microwave sintering. Finally effect of sintering on the structural and electrical studies was carried out.

EXPERIMENT

Li$_{0.4}$ Ni$_{0.2}$ Fe$_{2.4}$ O$_4$ (LNF) was synthesized by the citrate precursor method. The starting chemicals used were lithium nitrate, LiNO$_3$ (Merck, Germany), nickel nitrate, Ni (NO$_3$)$_2$.6H$_2$O (Merck India), iron nitrate nonahydrate, Fe (NO$_{3)3}$.9 H$_2$O (Merck, India) and citric acid monohydrate, C$_6$H$_8$O$_7$ (Merck, India). Appropriate amount of lithium nitrates, nickel nitrate, iron nitrates and citric acid were mixed together to make a solution. Metal ion and citric acid are taken in the ratio of 1:1. The resulting solution was refluxed at 40°C and

ammonia solution is added to maintain the pH value at 7.The pH controlled solution was then put in an oven at 100ºC. Finally auto combustion takes places forming ash which is the required ferrite material. The ash prepared ferrite powder was mixed with polyvinyl alcohol as a binder and pressed into pellets. Then AP pellets samples was given conventional and microwave sintering at the same temperatureof 500º C(CS sample for 3 hr at a heating rate of 5ºC/min, MS sample for 10 min at a heating rate of 10ºC/min). Spinel phase structure of all the samples was identified by X Pert Pro X-ray diffractometer using Cu-Kα radiation of incident wavelength λ=1.5405 Aº. By using XRD data, the lattice constant was calculated using the formula

$$a = d_{hkl}(h^2 + k^2 + l^2)^{1/2} \tag{1}$$

where 'a' is the lattice constant,'d' is the interplanar spacing and h, k, l are the miller indices.

Theoretical density was calculated by using the relation

$$d_{xrd} = \frac{8M}{Na^3} \tag{2}$$

where $d_{xrd}$is the theoretical density; M is the molecular weight of the samples, N is the Avogadro number and a is the lattice constant of the sample.

Experimental density was measured using the formula

$$d_{expt} = \frac{Mass}{Volume} \tag{3}$$

and porosity was also calculated using the relation

$$P\% = \frac{d_{xrd} - d_{expt}}{d_{xrd}} \tag{4}$$

where d_{xrd} is the theoretical density and d_{expt} is the experimental density of the samples.

Using Debye Scherer's formula, crystallite size was calculated using the formula

$$D_{cryst} = \frac{0.89\lambda}{\beta cos\theta} \tag{5}$$

where λ is the wavelength ofCuK$_\alpha$ radiation, β is the full width at half maximum.

The capacitance and quality factor was measured by using Agilent E4980 Precession LCR meter in the frequency range of 20Hz-2MHz.Then the dielectric constant ε' was calculated using formula

$$\varepsilon' = \frac{Cd}{\varepsilon_o A} \tag{6}$$

where d is the thickness of the sample $\varepsilon_o$is the absolute permittivity of free space and A is the area of the sample.

and dielectric loss tangent (tanδ)was calculated using the formula

$$tan\delta = \frac{1}{Q}, \text{ where Q is the quality factor.} \tag{7}$$

Room temperature dc resistivity of the three samples were calculated using the relation

$$\rho = \frac{R A}{l} \tag{8}$$

where R is the resistance of the samples, A is the area of the sample and l is the thickness of the samples.

RESULT AND DISCUSSION

XRD analysis

Fig.1a depicts the XRD patterns of the AP and CS samples and Fig.1b depicts XRD patterns of AP and MS samples. The observation shows diffraction peaks corresponding to the lattice planes of (220), (311), (400), (422), (511), (440) etc. for AP as well as sintered samples and is well matched with the standard JCPDS card [7] . No extra peak due to impurities is present. It confirms the spinel phase formation of all the samples. The formation of spinel phase in ash prepared sample without sintering reveal that the LNF can be synthesized at a very low temperature using the citrate precursor method.
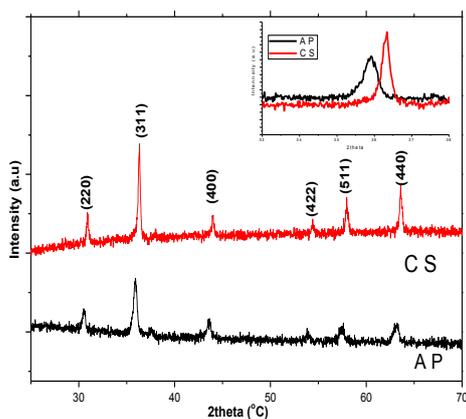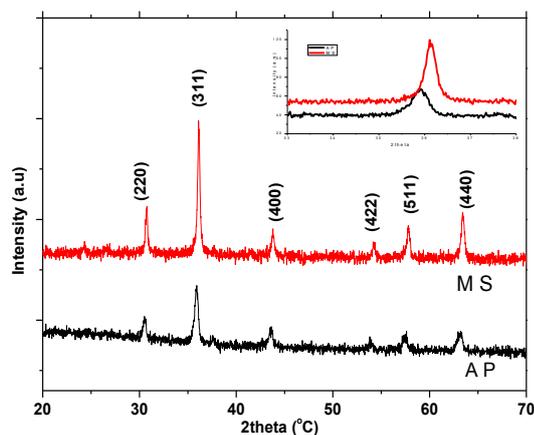

Fig. 1a. XRD patterns of AP and CS samples

Fig. 1b. XRD patterns of AP and MS samples

From the XRD data the lattice constant (a), theoretical density (D_{XRD}) crystallite size (D_{cryst}) of AP and sintered samples were found out. The values of lattice constant for AP, CS and MS were 8.410 A°, 8.370A° and 8.372 A° respectively. This lower value of lattice constant in sintered samples as compared to AP samples may be attributed to the decrease in unit cell volume of the samples. It was supported by the shifting of position of theXRD peak considering a typical peak of (311) shown in inset of both the figures. Peak position is assumed to shift to higher angles with decreasing lattice constant as was reported earlier by several workers. Also sharp intensity peak is observed in case of sintered samples as compared to AP sample. This is again supported by the higher crystallite size and there was report earlier by other workers that higher crystallite size show sharper peak [8].

The value of both theoretical and experimental density is higher in sintered samples as compared to AP sample. These may be due to the fact that during sintering process force is being generated by the thermal energy which drives the grain boundaries to grow over pores reducing the porosity in the sintered samples which further densifies the material. It is supported by the increase in crystallite sizes of sintered samples which again relate to increase densification.

However considering the two type of sintering techniques CS and MS, lattice constant is higher in MS samples. Also as was discussed above the higher the lattice constant the lower the crystallite size. In the present study crystallite size is lower in MS sample, hence a higher lattice constant. Density is higher in CS sample compared to MS sample. The possible reason maybe the duration given in MS is very low and needs an optimum temperature [9]. However detailed investigation on this two technique is required. .

Table 1: Density (theoretical and experimental), porosity, crystallite size, dielectric constant and DC resistivity of AP, CS and MS samples

Sintering	d_{XRD} (gm/cm³)	d_{expt} (gm/cm³)	Porosity P (%)	D_{cryst} (nm)	Dielectric constant $\varepsilon' \times 10^2$	DC resistivity $\rho_{dc} \times 10^7$ (Ohm-cm)
AP	4.74	3.66	22	20	8.63	15.10
CS	4.81	3.80	21	25	2.63	18.22
MS	4.81	3.77	21	24	1.70	19.12

FTIR spectra:

Fig.2 depicts the FTIR spectra of AP, CS and MS samples. It is generally known that the spinel ferrite exhibit three characteristics absorption bands (υ_1, υ_2 and υ_3).In present investigation, two main IR absorption bands (υ_1 and υ_2) appeared in the present AP, CS and MS samples between the wave number 370cm⁻¹- 590cm⁻¹.
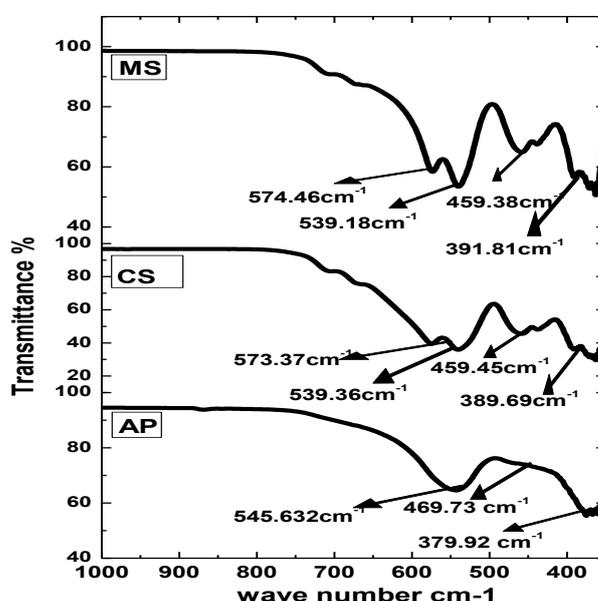

Figure 2: FTIR spectra of (a) AP (b) CS and (c) MS LNF samples

The high absorption bands (υ_1 and υ_2) of all samples lies in the wave number ranges from 540-575cm^{-1} and 375-392cm^{-1} respectively. These strong bands arises due to the metal-oxygen (Fe^{3+}-O) stretching at tetrahedral and octahedral sites in spinel ferrite samples[10]. Here it is seen that the intensity value of υ_1 is higher than that of the υ_2 which indicates that the normal mode of metal-oxygen vibration of tetrahedral sites is higher than that of the vibration at octahedral sites. This may be attributed to the fact that the bond length of Fe-O (1.89 A^{o}C) at tetrahedral sites is shorter than that of the bond length of Fe-O(1.99) at octahedral sites[11]. Another shoulder bands of high absorption bands around 539.36cm^{-1} and 539.18cm-1 appeared in the CS and MS samples at tetrahedral sites and such bands is   denoted by υ_1 (s). This may be due to the presence of Fe^{2+} ions which produces the splitting of absorption bands and thus this causes Jahn tellar distortion. Another weak band υ_2 had appeared in the lower wave number 459-469cm^{-1}.This bands is caused due to Li-O stretching vibration [12]. On comparing of AP and sintered samples (CS and MS), the bands position (υ_1 and υ_2) is shifted (blue shift) to higher wave number. It is reported by other workers that increasing the sintering temperature shift the peak towards higher wave number. Also the increase in sintering temperature increases the crystallite size [13]. In the present study the crystallite size is higher in the sintered samples and hence a shift in the higher wave number is expected and is observed experimentally.

Electrical studies

Fig.3 shows the frequency variation of dielectric constant (ε') for AP and sintered samples. It is observed that dielectric constant decreases with increasing frequency of the applied field and then remains constant at high frequency.
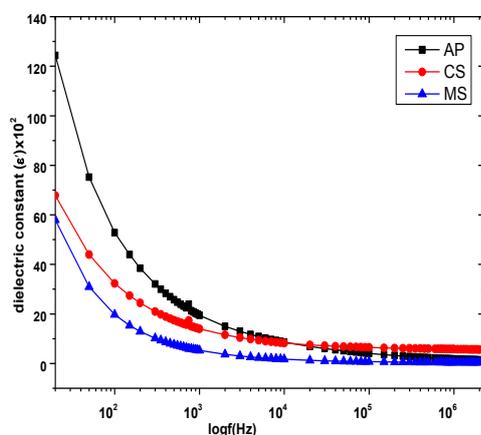

Figure 3: Dielectric constant vs frequency of (a) AP (b) CS and (c) MS LNF samples

This behaviour was explained on the basis of space charge polarization and Koop's two layers model [14]. According to the model, it is assumed that the dielectric structure of ferrite consists of two layers separated with each other. One layer is a well conducting grains while other is a poorly conducting grain boundaries. The dielectric is further related to polarization. Polarization of ferrite material is contributed mainly by four primary mechanisms such as electronic polarization, atomic polarization, dipole polarization and interfacial or space charge polarization. The former two mechanisms contribute polarization to the material at the higher frequency (10^{12}-10^{15}Hz) whereas the latter two mechanism to that of the lower frequencies ($<10^{12}$ Hz). The mechanism of polarization in ferrites is considered to be similar to that of electrical conduction process. The electrical conduction process may be explained by Verwey mechanism of electron hopping between Fe^{2+} and Fe^{3+} at the octahedral sites [15]. This hopping of electrons give the local displacement of electrons in the direction of an applied field thereby inducing polarization. At low frequency of external applied ac field, high resistive grain boundaries hinders the hopping motion of electrons. This results in piling up of electron at the grain boundaries which contribute to space charge thereby inducing space charge polarization and therefore dielectric constant is higher in low frequency region. By increasing the frequency of the field, electron hopping is not be able to follow the direction of applied field , hence electron reverse the direction of motion thereby reducing the possibility of electron hopping. This leads to decrease in the value of dielectric constant. At still higher frequency, the dielectric constant becomes almost independent of frequency [16].

Comparing AP and sintered samples the value of dielectric constant is lower in sintered samples [7]. When sintering is given to the AP samples, the density of the samples increases so that crystallite size increases as was explained in the previous part. This results in higher surface to volume ratio such that oxidation takes place slower i,e slow conversion of Fe^{3+} to Fe^{2+} ion. Hence there is less existence of Fe^{2+} ion which is responsible for conduction process. Ultimately it suppresses the exchange of electrons thereby decreasing the value of dielectric constant in the sintered samples [17].

Further taking into account CS and MS samples dielectric constant is lower in MS samples which may be due to the less formation of ferrous ion. This may be is attributed to the less duration of time given during sintering as compared to conventional sintering. Here the density and crystallite size could not support the result as the variation is almost negligible. However further investigation on sintering duration is needed.

Fig 4 depicts the frequency variation of dielectric loss tangent for AP, CS and MS samples.The dielectric loss tangent decreases with increasing frequency of the applied field and then becomes constant for higher frequency of the applied field. This is in good agreement with that of the other workers [18-19].
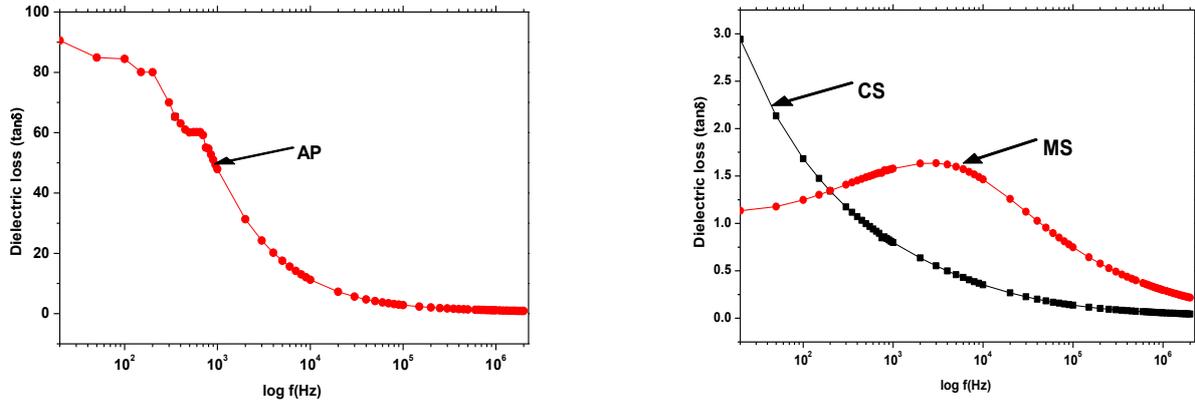
Figure 4: Dielectric constant vs frequency of (a) AP and (b) CS and MS samples

Comparing AP and sintered samples (CS and MS) CS and MS samples show low dielectric losses. Dielectric loss is referred to expenditure of energy to store capacitance of the material. If the conduction is large there will be large leakage current giving more energy loss [20].When sintering is given densification increases resulting in less conduction which further decreases the energy loss. In the present study, conduction is high in AP samples and therefore more leakage current is produced thereby increasing the loss of energy. Thus a high dielectric loss is observed in AP samples.

However on comparing CS and MS samples, a very low losses is found in microwave sintered samples.This is because of the fact that in microwave sintering takes less time i.e only 10 minutes and rapid heating rate of $10^oC/min$ is given. In MS samples resonance peak could be observed. It is known that maximum energy is stored when hopping frequency of electrons between ferrous and ferric ions at the B-site match to that of the applied field frequency which appears in the form of resonance peak. In the present study for the other samples AP and CS the peak might have shifted to higher frequency whereas for MS sample it is observed at a much lower frequency compared to the other two. The possible reason for shifting peak towards lower frequency can be explained on the basis of Debye's relaxation theory. Accordingly, a dielectric loss peak occurred when the frequency of the applied field is equal to that of the hopping frequency satisfying condition $\omega\tau = 1$ where $\omega = 2\pi f_{max}$ and τ is the relaxation time. The relaxation time being related to hopping frequency and then to the hopping probability per unit time P as f $_{max} = (1/\pi)P$ [21]. As the probability of electron hopping is lowest in MS sample as was explained above there is a decrease in frequency and hence peak shift towards lower frequency [22]. This is supported by the lowest value of dc resistivity in MS sample compared to AP and CS samples.

CONCLUSION

$Li_{0.4}Ni_{0.2}Fe_{2.5}O_4$ was successfully synthesized by citrate precursor method. XRD patterns of AP, SS and MS samples confirmed the formation of spinel phase. FTIR analysis shows existence of two strong bands and one weak band, a characteristic of spinel ferrite. The sintered samples show higher densification, higher crystallite size and lower porosity as compared to AP samples. Electrical studies revealed that the dielectric constant, dielectric loss are lower in sintered samples as compared to AP samples. The lower dielectric constant is explained due to the suppression of exchange electrons which results from higher surface to volume ratio a consequence of increase crystallite size. A resonance peak could be observed in MS samples only. This was explained on the basis of Debye relaxation theory such that probability of electron hopping is lowest in MS resulting in decrease frequency. Hence peak shift towards lower frequency which is being supported by the observance of lowest dc resistivity among the three samples. For the other two sample the peak might be in higher frequency region which need investigation in future works.

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