

## Effect of Heat Treatment on the Electrical and Magnetic Properties of $\text{Li}_{0.45}\text{Mn}_{0.1}\text{Fe}_{2.45}\text{O}_4$ Ferrite

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**Abstract:** Ferrite with the composition  $\text{Li}_{0.45}\text{Mn}_{0.1}\text{Fe}_{2.45}\text{O}_4$  was prepared using the citrate precursor method. The sample was given final sintering at five different temperatures of 1080°C, 1032°C, 984°C, 936°C and 888°C after a pre sintering at 540°C. The final heating rate of the samples is 6°C/min. Spinel structure of the prepared ferrite sample was confirmed from the X-ray diffraction technique. From the analysis of the XRD data, parameters such as density, and crystallite size were calculated. With the increase in the sintering temperature the theoretical and the experimental densities were observed to increase, the experimental density being determined using the Archimedes's principle. The crystallite size for the samples was in the nanometer range. Room temperature dc resistivity and room temperature dielectric constant at 10 kHz were investigated. The dc resistivity increases while the dielectric constant shows a decrease with the rise in the sintering temperature. Dispersion is observed in the variation of dielectric constant with frequency. The Curie temperature shows a decrease. Possible reason for all the above observation is being discussed

**Keywords:** Ferrites, Citrate precursor, XRD, Dielectric constant, DC resistivity, Curie temperature

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## 1. Introduction

Lithium based ferrite are widely studied material but the interest continues due to their various technological applications. They are found to be used in certain devices like transformer, microwave devices, electronic and magnetic components<sup>1-3</sup> etc due to their properties like high resistivity, high magnetization, high Curie temperature, good hysteresis properties, low initial permeability etc<sup>4-7</sup>. The properties are dependent on many factors like substitution, synthesis and sintering. There are two broad synthesis methods; the conventional and the non conventional method. The non conventional method is preferred as the former method has several drawbacks including chemical inhomogeneity etc. In non conventional method there is advantage of low temperature sintering. There are many non conventional methods such as citrate precursor method, chemical co precipitation, hydrothermal, sol gel method etc<sup>8-10</sup>. Among them the citrate precursor method is preferred as it involves short duration of time, simple and economic.

In this paper the effect of sintering at different temperatures on various electrical and magnetic properties of  $\text{Li}_{0.45}\text{Mn}_{0.1}\text{Fe}_{2.45}\text{O}_4$  is being investigated

## 2. Experimental Details

Manganese substituted lithium ferrites with the formula  $\text{Li}_{0.45}\text{Mn}_{0.1}\text{Fe}_{2.45}\text{O}_4$  was synthesized by the citrate precursor method. The starting precursors used were lithium nitrate, manganese acetate, iron nitrate and citric acid. Stoichiometric amount of lithium nitrate, manganese acetate, 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 had been reported earlier<sup>4</sup>. The synthesized powder was mixed with a binder and pressed into pellets with 50 kilo Newton pressure. The samples were pre-sintered at 500°C followed by a final sintering in air at five different temperatures of 888°C(F<sub>1</sub>), 936°C(F<sub>2</sub>), 984°C(F<sub>3</sub>), 1032°C(F<sub>4</sub>) and 1080°C(F<sub>5</sub>) for 3 hours. From the XRD data of the final sintered sample the theoretical density and crystallite size was calculated. Archimedes's principle was used to measure the experimental density. Dielectric constant at room temperature was studied as a function of sintering temperature and frequency (20Hz-1MHz). The measurement was carried out using an Agilent HP 4284A LCR meter and the value of dielectric constant was calculated using the formula  $\epsilon' = Cd / \epsilon_0 A$  where C is the measured capacitance, d the thickness, A the cross sectional area of the sample and  $\epsilon_0$  the permittivity of free space. The dc

resistivity at room temperature was measured using four probe method. The Curie temperature was measured using the Soohoo's method.

### 3. Results and Discussion

XRD pattern was used to confirm the spinel phase structure of the  $\text{Li}_{0.45}\text{Mn}_{0.1}\text{Fe}_{2.45}\text{O}_4$  ferrite 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 signifying that there is no impurity present. A typical XRD for  $\text{Li}_{0.45}\text{Mn}_{0.1}\text{Fe}_{2.45}\text{O}_4$  which was final sintered at  $1032^\circ\text{C}$  is shown in Fig.1.

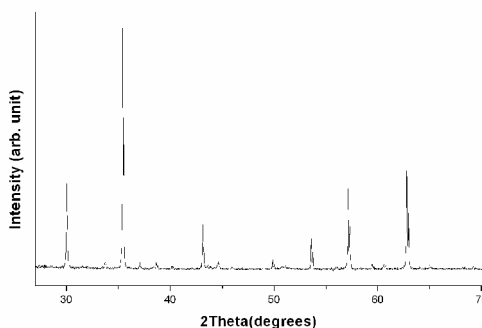


Fig.1 XRD for  $\text{Li}_{0.45}\text{Fe}_{2.45}\text{Mn}_{0.1}\text{O}_4$  final sintered at  $1032^\circ\text{C}$

The densities of the samples as measured experimentally and those calculated from the XRD data are tabulated in Table 1. An increase is observed with the increase in sintering temperatures. These results are in agreement with the observations of previous workers<sup>11-12</sup>.

Table1. Density (theoretical and experimental), Porosity, Crystallite size and Curie temperature of  $\text{Li}_{0.45}\text{Fe}_{2.45}\text{Mn}_{0.1}\text{O}_4$

| Sample No.     | Theo.density (g/cc) | Expt. Density (g/cc) | Porosity (%) | Crystallite size (nm) | Curie Temp. ( $^\circ\text{C}$ ) |
|----------------|---------------------|----------------------|--------------|-----------------------|----------------------------------|
| F <sub>1</sub> | 3.75                | 4.69                 | 20           | 300                   | 633                              |
| F <sub>2</sub> | 3.83                | 4.80                 | 20           | 310                   | 631                              |
| F <sub>3</sub> | 3.88                | 4.83                 | 19           | 400                   | 629                              |
| F <sub>3</sub> | 4.05                | 4.94                 | 18           | 468                   | 623                              |
| F <sub>4</sub> | 4.13                | 4.98                 | 17           | 521                   | 621                              |

The densities of the samples calculated from the XRD data and those

measured experimentally are tabulated in Table 1. An increase is observed with the increase in sintering temperatures. These results are in agreement with the observations by previous workers<sup>13-15</sup>. The porosity shows a decreasing trend with increase in the sintering temperature and is in the range of 17%-20%. It has been calculated using the formula

$$P(\%) = \frac{\rho_{\text{theo}} - \rho_{\text{expt}}}{\rho_{\text{theo}}},$$

where  $\rho_{\text{theo}}$  is theoretical or XRD density and  $\rho_{\text{expt}}$  is experimental density. The increase in densification may be due to the shrinking of the pores. Hence the decrease in the porosity is expected. The crystallite size was calculated from the XRD data using the Debye Scherrer formula given by, Crystallite size =  $0.9\lambda/\beta \cos\theta$  where  $\lambda$  is wavelength,  $\beta$  is full width at half maximum.

It is observed that with the increase in sintering temperature it shows an increasing trend. This is because the increase in density increases slowly in the crystallite size.

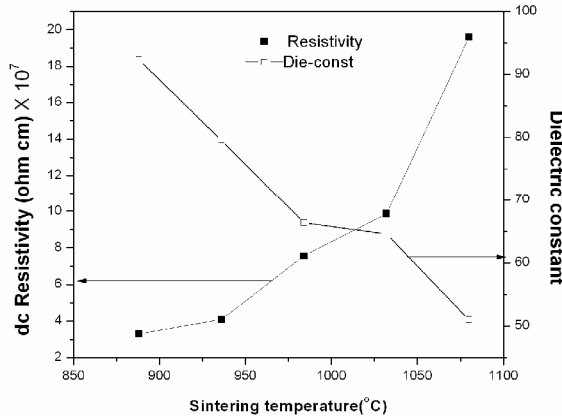


Fig.2 Variation of dc resistivity and dielectric constant with sintering temperature

Fig. 2 shows the variation of the dielectric constant and dc resistivity at room temperature with sintering temperature. It is observed that the dielectric constant decreases while the dc resistivity increases with the increase in the sintering temperature. The decrease in the dielectric constant can be explained on the basis of space charge polarization and Koop's two layer model<sup>13-16</sup>. 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  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions at B sites. The electrons reach the grain boundary by hopping and pile up due to its higher resistivity. This produces the space charge polarization. However in the present study there is a decrease in the dielectric constant with increasing temperature. These may be due to decrease of charge mobility carrier with increasing sintering temperature. During oxidation in air at the time of sintering  $\text{Fe}^{2+}$  ion may be converted into  $\text{Fe}^{3+}$  ion suppressing the exchange of electron as was reported by other workers<sup>13,15</sup>. Thus a decrease in the dielectric constant is observed with increase in sintering temperature.

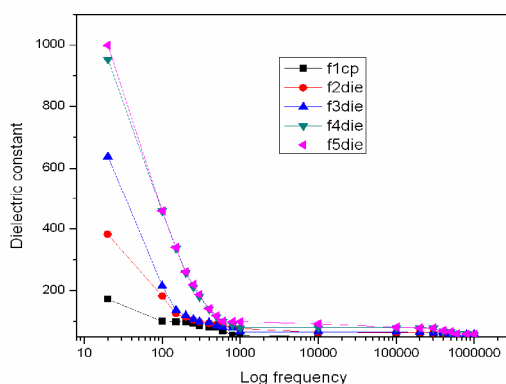


Fig. 3 Variation of dielectric constant with frequency

The frequency dependence of dielectric constant is shown in Fig. 3. It is observed that the dielectric constant shows dispersion with increasing frequency which is a normal behavior of ferrites. At low frequencies the value of dielectric constant is high, and then 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. 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<sup>16-20</sup>.

The room temperature dc resistivity is observed to increase with the increase in the sintering temperature which may be due to decrease of charge mobility carrier with increasing sintering temperature. During oxidation in air at the time of sintering  $\text{Fe}^{2+}$  ion may be converted into  $\text{Fe}^{3+}$  ion suppressing the exchange of electron as was mentioned above.

The measured Curie temperature obtained for different sintering temperature is shown in Table 1. It is observed in the table that the Curie temperature decrease with increase in the sintering temperature. This may be due to weakening of the magnetic exchange interaction with the increase in the sintering temperature<sup>21</sup>.

#### 4. Conclusions

$\text{Li}_{0.45}\text{Mn}_{0.1}\text{Fe}_{2.45}\text{O}_4$  has been successfully prepared by the citrate precursor method. Densification is more with the increase in sintering temperature while the porosity decreases. The dielectric constant at room temperature decreases with increase in sintering temperature whereas the dc resistivity at room temperature shows an increase. 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. The Curie temperature is observed to decrease with the increase in the sintering temperature.

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